

FORMATION OF ACTIVE SITES ON IRON CATALYST

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Abstract

Fischer-Tropsch synthesis over preliminary carburized iron catalyst with CO was investigated in both isothermal and temperature programmed experiments under atmospheric pressure. In comparison with the freshly reduced catalyst, the pre-carburized catalyst showed similar activity for the formation of hydrocarbons at the steady state and shorter period of activation which decreased with the degree of carburization. The pre-carburization was observed to reduce the strength and to raise the amount of the CO adsorption. Since no significant differences were observed between the carburizations with CO/He and CO/H₂, it was confirmed that the role of the carburization during synthesis was not the formation of reaction intermediates but the development of the active surface available for catalysis.

Introduction

In the last decade, the catalytic conversion of coal into liquid and gaseous fuels is one of the most possible means in order to solve the energy problem. From this point of view, Fischer-Tropsch synthesis has been considered to be an attractive process and investigated by many researchers in the world. The mechanism of this synthesis is, however, still obscure.

It has been well recognized that transition metal catalysts transform to their carbides during the synthesis. Roles of the carbides are now the subject of much speculation and experiment. The author (1-8) have already suggested that the carburization of a fused iron catalyst during synthesis play an important part in the development of active surface available for the catalysis. The similar proposals were provided independently by Amelse, Butt and Swartz (9) and by Raup and Delgass (10). It has been widely spread theory, on the other hand, that carbidic carbon itself is the reaction intermediates in the formation of hydrocarbons. This theory was proposed first by Fischer and Tropsch (11) and supported recently by Araki and

Ponec (12). The objective of the present work is not to engage in details of the reaction mechanism but to confirm the former proposal. The confirmation was made by the comparison of catalytic behaviors of preliminary carburized iron with those of metallic iron.

Experimental

Fischer-Tropsch synthesis, decomposition of carbon monoxide and temperature programmed desorption of CO over a fused iron catalyst were carried out under atmospheric pressure. These reactions were simultaneously followed by temperature programmed gravimetry (TG), differential thermal analysis (DTA), gas chromatography (GC) and mass spectrometry (MS).

The catalyst basket of platinum in a quartz reactor was held in an infrared image furnace controlled by a programming unit. A platinum-rhodium thermocouple was located in the middle of the catalyst to measure its temperature with the accuracy of $\pm 0.5^\circ\text{C}$. The maximum sensitivity of TG (Ulvac, TGD-3000H) was $1\ \mu\text{g}$. Analysis of the reaction products was carried out continuously by MS (Ulvac, MSQ-150) with a multi-channels programmer and occasionally by GC (Poropak Q column) with a flame ionization detector.

In most isothermal experiment of this work, feed rates of CO/H_2 and CO/He were explored between 7.4 and 7.7 ml min^{-1} over the original iron oxide of $100 \pm 0.3\ \text{mg}$. The computation of the reaction rate was simplified in accordance with the method described elsewhere(2). In the experiments of temperature programmed desorption (TPD) of adsorbed CO, a quartz coated tubular reactor with 500 mg of the original oxide was used in $8.6 \pm 0.1\ \text{ml min}^{-1}$ of helium stream because of poor adsorptive property of the fused iron catalyst. The reaction temperatures employed in the continuous experiment and the TPD were 250°C and $25\text{--}800^\circ\text{C}$, respectively.

The iron catalyst used in the present work was CCI fused magnetite (1, 2) for ammonia synthesis with the composition: Fe_3O_4 , 96.5; Al_2O_3 , 2.5; K_2O , 0.6 and SiO_2 , 0.4%. The particle size of the catalyst examined ranged from 250 to 300 μm . Prior to the reactions, the magnetite was reduced in a hydrogen stream for a period of 30 h at 550°C . According to the measurement of weight decrease by TG and diffraction pattern by X-ray analysis, the magnetite converted almost completely to α -iron by this reduction. The specific surface area of the reduced catalyst was determined to be 18.0

m^2g^{-1} by the BET method. The reactant mixture used in Fischer-Tropsch synthesis and CO decomposition were 10.0% CO in H_2 and 10.1% CO in He, respectively, stored in high pressure cylinders. Hydrogen used was ultra high pure hydrogen.

Results

It is widely recognized fact in Fischer-Tropsch synthesis that iron catalysts show long periods of activation in the formation of hydrocarbons. After the reduction, the catalyst was cooled to room temperature and subsequently evacuated for 30 min prior to exposure to the reactant mixture. When a constant flow of the reactant stream was obtained, the catalyst was rapidly heated to the reaction temperature of 250°C in 1 min. The freshly reduced iron showed little catalytic activity in the hydrocarbon formation. As shown in Fig. 1, rates of the CH_4 (thin solid curve) and C_2H_6 (thin broken curve) formations increased gradually with time on stream, until steady states were obtained in about 150 min after the synthesis started. Using 10% CO in H_2 as the reactant, this commercial catalyst showed no appreciable decrease of activity for the hydrocarbon formation in the steady states. This is one of the reasons why CCI fused magnetite

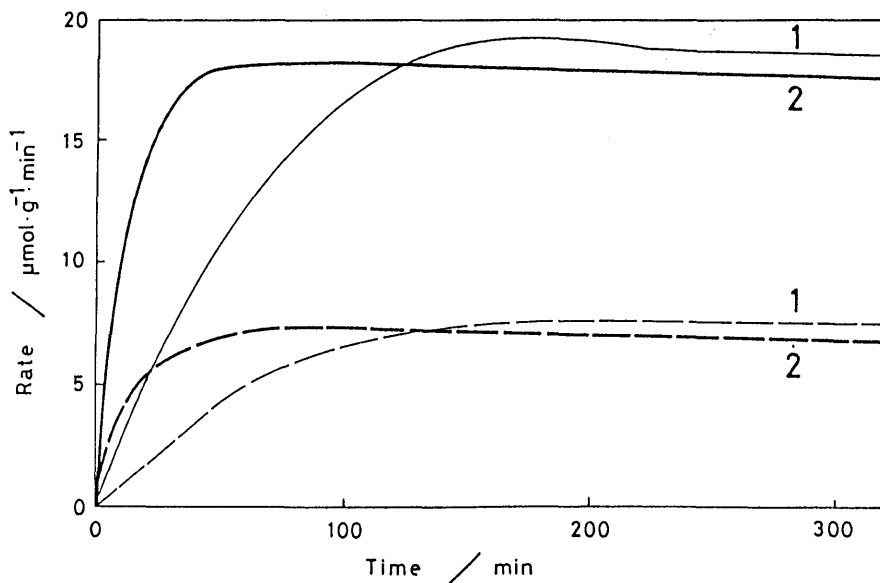


Fig. 1 Time dependences in formation of CH_4 (solid curve) and C_2H_6 (broken curve) over fresh (1) and pre-carburized catalysts.

and diluted CO were employed as the catalyst and the reactant, respectively. Unpromoted iron catalysts prepared in laboratories are, in general, so unstable that distinct steady states are difficult to consider (13). Other higher hydrocarbons, such as C_3H_8 and C_4H_{10} , were formed in the similar manner. Only CH_4 and C_2H_6 were analyzed accurately as hydrocarbon products in this work. On the other hand, no appreciable such periods of rate increase were observed in the formations of H_2O and CO_2 (2, 3, 8) which were another main products of the synthesis. Rates of the H_2O and CO_2 formations decreased slowly with time on stream.

The catalytic behavior of iron is strongly influenced by a preliminary carburization which is done by means of decomposition of CO to CO_2 and carbon. The pre-carburization was carried out as follows. After the reduced catalyst was evacuated for 30 min at room temperature, 10% CO in He was introduced to the reactor. Recognizing a constant flow of the stream, the catalyst was heated to $250^\circ C$ in 1 min. The treatment with CO/He was continued for 140 min and gave 33.5 mg g^{-1} of weight increase of the catalyst. During this pre-treatment only CO_2 was observed as the gaseous product. After the pre-carburization, activity test of the catalyst was examined in the similar way to that of the fresh catalyst. The result is also shown in Fig. 1. No significant differences in the steady state rates of the hydrocarbon formation were observed between the pre-carburized (thick curves) and the fresh (thin curves) catalysts. However, the activation period for the former was only 50 min whereas that for the latter was 150 min. The preliminary carburization reduced appreciably the H_2O and CO_2 formations in the early period of synthesis. Rates of the H_2O and CO_2 formations over the pre-carburized catalyst gradually approached to those over the fresh catalyst with time on stream.

Figure 2 shows the results of DTA (a) and TG (b) measurements during the synthesis (thin curve) and the pre-carburization (thick curve). In CO/H_2 stream, weight of the catalyst increased rapidly in the early stage and then slowly. The weight increase continued even after 150 min where the formation of hydrocarbons attained to the steady states. Weight increase in the CO/He stream proceeded in the similar manner, although its rate was smaller than that in the CO/H_2 stream. The results of DTA for both treatments (in an arbitrary scale) showed that large heats were generated at initial periods of the treatment. The exothermic reactions decreased slowly with time on streams. The heat generation in CO/He stream was much smaller than that in CO/H_2 stream.

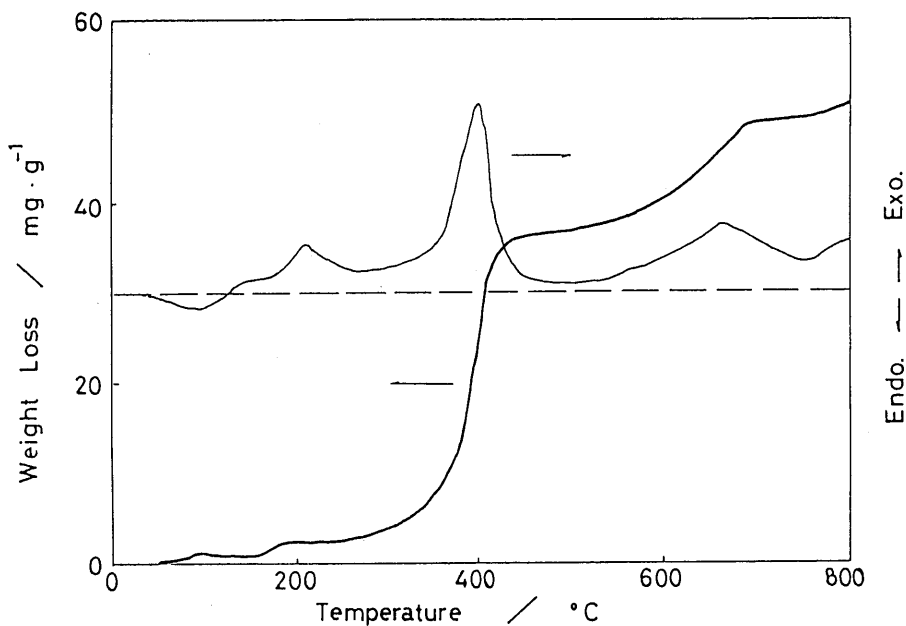


Fig. 2. TG-DTA results of the catalyst during programmed reduction.

Thick curve, TG and thin curve, DTA.

Measurements of X-ray were examined to check the carbide formation during the synthesis and the CO decomposition. The results showed the similar diffraction patterns in which all predominant peaks were corresponded to $\text{Fe}_{2.5}\text{C}$ and $\alpha\text{-Fe}$. The existences of other carbides, such as $\text{Fe}_{2.2}\text{C}$ and Fe_2C , were not recognized well in the present work, while several carbides were reported in the case of supported iron catalysts (14, 15).

In order to study the relation between the catalytic activity and the carburization, rates of the hydrocarbon formation were measured over the catalyst with various degrees of carburization. The pre-carburizations of catalyst were carried out with 10% CO in He for various periods at 250°C . The results are shown in Fig. 3 and 4, respectively, for CH_4 and C_2H_6 . In these figures, the rates are plotted against the weight increase of catalyst during the synthesis as well as during the pre-carburization. Both rates of the CH_4 and C_2H_6 formations over the fresh catalyst (curve 1) increased almost proportionally with the increase of catalyst weight up to 50 mg g^{-1} . Further increase of the weight showed virtually no effect on the catalytic activity.

Weight increases of the catalyst carburized preliminarily for 100 (curve 2), 140 (3), 260 (4) and 400 (5) min were 26.2, 33.5, 49.0 and 58.0 mg g^{-1} ,

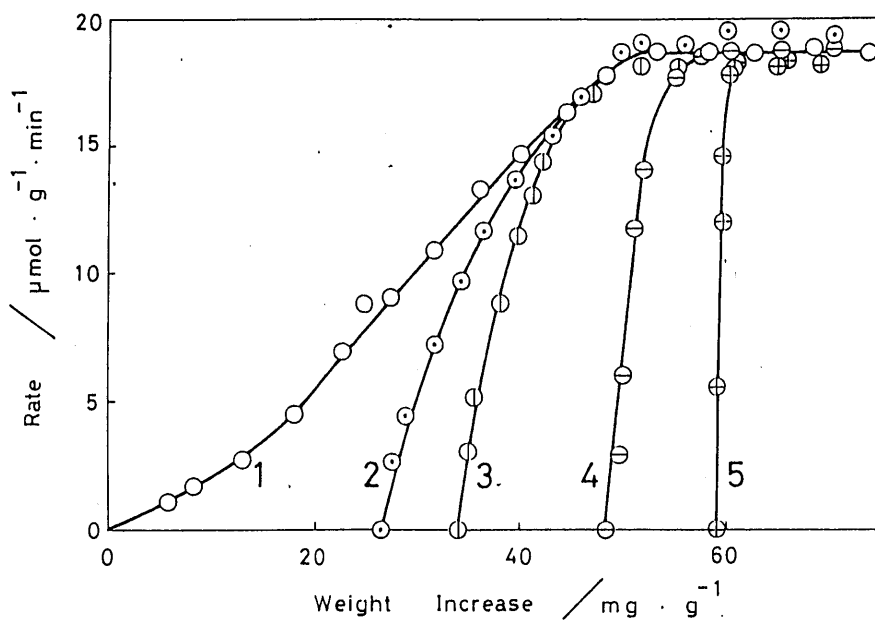


Fig. 3 Effects of Pre-carburization on CH_4 formation.
 Period of CO treatment : 1,0 ; 2,100 ; 3,140 ;
 4,260 ; 5,400 min

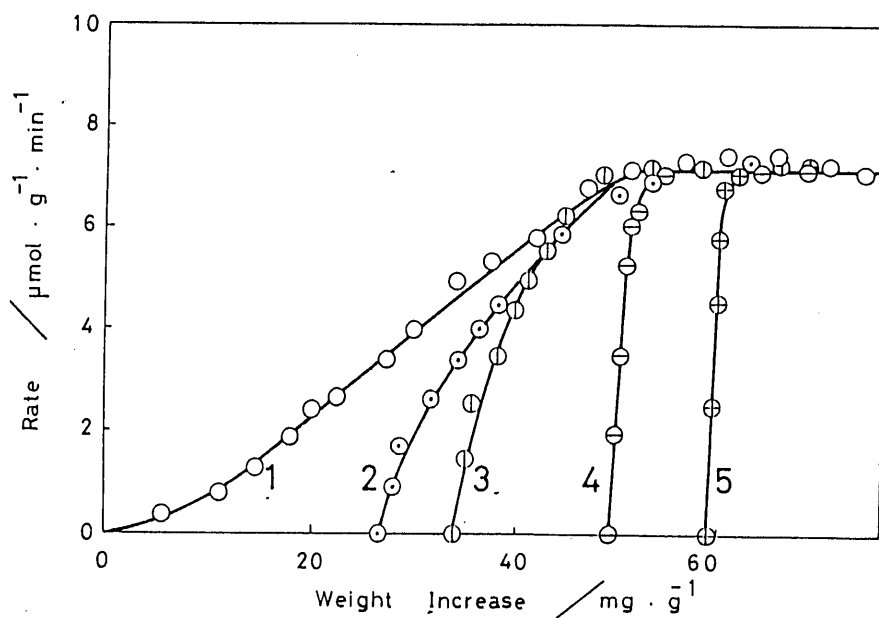


Fig. 4 Effects of pre-carburization on C_2H_6 formation.
 Period of CO treatment : 1,0 ; 2,100 ; 3,140 ;
 4,260 ; 5,400 min

respectively. These values are shown on the abscissa of Fig. 3 and 4. As indicated in these figures, no appreciable difference of the steady state activity was observed among these catalysts. The catalysts carburized with CO/He for 100, 140, 260 and 400 min showed about 90, 50, 30 and 30 min of activation periods, respectively. Rates of the hydrocarbon formation over the catalyst with lower degrees of carburization (curves 2 and 3) increased sharply and coincided with that over the fresh catalyst (curve 1) as the reaction proceeded. The increases of rate over the highly carburized catalysts (curves 4 and 5) were almost vertical against the weight increase during synthesis.

Experiments of TPD of adsorbed CO were performed for both the fresh and the carburized catalysts. Prior to the TPD measurements, the catalysts were treated as follows. The reduced catalyst was carburized in a stream of 10% CO in He or 10% CO in H₂ for 100 min at 250°C. After the catalyst was flushed with pure helium, it was saturated with pure CO for 1 h at room temperature. The saturated catalyst was again flushed with pure helium for 3 h at room temperature in order to remove physically adsorbed CO from the surface and then the TPD was examined in He stream at the heating rate of 3°C min⁻¹.

Heating these catalysts yielded only CO and CO₂ desorptions. Figure 5 shows the CO desorption spectra of CO adsorbed on iron carbides prepared by CO/He treatment (thick solid curve) and by CO/H₂ treatment (thin solid curve), together with those of the fresh catalyst (broken curve). The CO desorption from the carburized catalysts consisted of three peaks from 200 to 400°C and a broad peak above 600°C. No significant differences in shape and temperature range of the desorption were observed between these two carburized catalysts. For the TPD spectra of the fresh catalyst, on the other hand, CO desorbed in three peaks from 400 to 600°C and no CO desorption was observed above 600°C where appreciable amounts of CO were detected in the case of the carburized catalysts. Figure 6 shows CO₂ desorption spectra of CO adsorbed on these three catalysts. For the catalysts carburized with CO/He (thick solid curve) and CO/H₂ (thin solid curve), CO₂ desorbed in large indistinct peaks near 200°C and small peak above 600°C. The desorption spectra of CO₂ for both carbides also bore remarkable resemblances. For the fresh catalyst, CO₂ desorbed in a single broad peak at an initial stage of the TPD and the higher temperature CO₂ above 600°C was completely absent.

Accumulated amounts of the CO and CO₂ desorption in the TPD meas-

Table 1 Effect of carburization on CO adsorption

State of catalyst	Amount of desorption (mol g ⁻¹)		Amount of CO adsorption (mol g ⁻¹)
	CO	CO ₂	
Freshly reduced iron	19.5	9.2	37.9
Carburized iron with CO/He	30.0	7.8	45.6
Carburized iron with CO/H ₂	34.4	17.3	69.0

urements are summarized in Table 1. Values of the table were calculated by integrating the corresponding curves in Figs. 5 and 6. The high temperature desorptions of CO and CO₂ above 600°C were excluded from the calculation, since the peaks did not finish in the TPD up to 800°C. It is suggested from Table 1 that the carburization of iron catalyst raised the amount of CO adsorption which is desorbed below 600°C as CO and CO₂. For these three kind of iron catalysts, about the half the adsorbed CO was decomposed to CO₂ and surface carbon. It has been reported in many works (16–18) that iron catalysts adsorb CO dissociatively even at room temperature. There is, however, few reports about CO₂ formation at such low temperatures.

Experiments of temperature programmed reduction (TPR) were carried

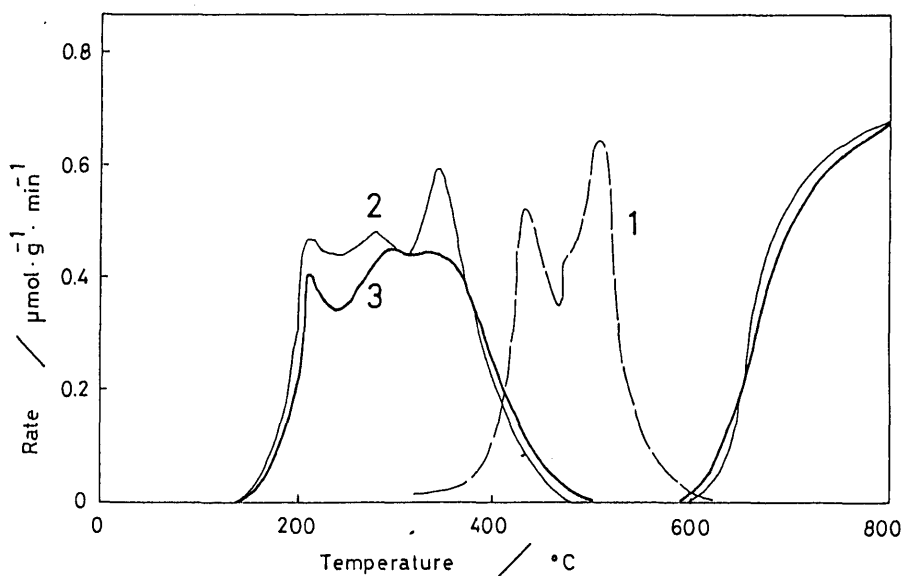


Fig. 5 TPD spectra of CO adsorbed on fresh (1), CO/H₂ treated (2) and CO/He treated (3) catalysts.

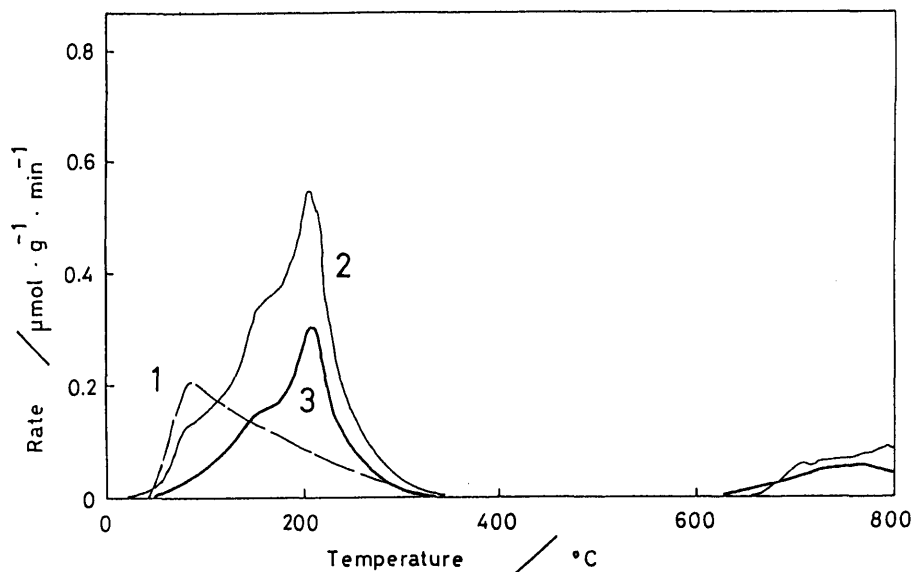


Fig. 6 TPD spectra of CO_2 for CO adsorbed on fresh (1), CO/H_2 treated (2) and CO/He treated (3) catalysts.

out for carburized catalysts. The reduced catalyst was separately carburized with CO/He and CO/H_2 at 250°C for 100 min. Heating these carbides in a stream of pure hydrogen at the rate of 2°C min^{-1} yielded CH_4 and small amount of H_2O as gaseous products. Neither CO nor CO_2 was detected during the TPR up to 800°C . It was indicative that higher hydrocarbons, such as C_2H_6 , C_3H_8 or C_4H_{10} , were completely absent in the TPR products. Both of the carbides obtained by the CO/He and CO/H_2 treatments showed almost similar spectra, although peak heights for the former was smaller than those for the latter. In these TPR, CH_4 formed in a single large peak near 400°C , whereas the H_2O formation consisted of two small broad peaks from 50 to 400°C and above 500°C .

Discussion

Rates of the hydrocarbon formation increased gradually with the increase of catalyst weight in the course of Fischer-Tropsch synthesis, although metallic iron showed little catalytic activity. In so far as the reactivity with hydrogen, the fused iron utilized in the synthesis contained one kind of carbon species which converted only to CH_4 near 400°C . The catalytic activity of iron, which once enhanced during the synthesis, was almost completely retained against repeated evacuations of the catalyst (3,

7). From these points of view, it can be elucidated that the carbon formation on (or in) the fused iron catalyst during the synthesis contributes not to the formation of reaction intermediates but to the development of active surface available for the catalysis.

From the X-ray diffraction patterns, fused iron utilized for the synthesis consisted primarily of α -iron and iron carbide corresponding to $\text{Fe}_{2.5}\text{C}$. Storch et al (19) reported that unpromoted and promoted iron catalysts formed ϵ -carbide (Fe_2C) and χ -carbide ($\text{Fe}_{2.5}\text{C}$), respectively, during the synthesis. Amelse et al (9) found the formation of ϵ' -carbide ($\text{Fe}_{2.2}\text{C}$) in addition to these carbides. In this work, the formation of $\text{Fe}_{2.5}\text{C}$ was recognized also by the treatment with CO/He. Since no appreciable difference in accumulated amounts was observed between CO_2 and carbon formation, the carburization of fused iron was considered to proceed via Boudouard reaction (20, 21) [disproportionation of CO to CO_2 and surface carbon]. As indicated in Fig. 2, rate of the carburization with CO/He was much smaller than that with synthesis gas. Turkdogan and Vinters (22) reported the similar promotive effects of hydrogen in the carbide formation on nickel catalysts. Since rate of the CO_2 formation during the synthesis was not closely dependent on the weight of catalyst, CO_2 was not simply a product of the disproportionation. Comparing to the DTA result for the CO decomposition, a large heat was generated during the synthesis (Fig. 2) because of exothermic formation of hydrocarbons. In the TPR experiments, both the catalysts treated with CO/He and CO/ H_2 gave only CH_4 as hydrocarbon product. This carbon species is supposed to be carbidic carbon of $\text{Fe}_{2.5}\text{C}$ [hydrogenated at 400°C] which is much more inactive than the reaction intermediates [hydrogenated easily at 250°C (1, 2)]. The carbidic carbon in the bulk phase, therefore, cannot be the reaction intermediates which give higher hydrocarbons.

The catalytic activity of iron increased almost proportionally with the increase in weight of catalyst and attained to stationary values, as shown in Figs. 3 and 4. The weight increase required for acquisition of the maximum rates was 50 mg g^{-1} in both of CH_4 and C_2H_6 formations. This value is smaller than expected values when iron phase of the catalyst is fully carburized to yield χ -carbide (86 mg g^{-1}), ϵ' -carbide (98 mg g^{-1}) or ϵ -carbide (107 mg g^{-1}). It has been reported that carburization of the bulk iron phase is incompleting even after 6 h of treatment with CO/ H_2 in the similar condition (10). Since the carburization proceeds from the surface into the bulk by the diffusion of carbon (23, 24) the surface available for catalysis

is considered to have been carburized enough by the amount of carbon which is much smaller than the expected values.

In the development of active surface of the fused iron catalyst, the preliminary treatment with CO/He showed the similar effect to the carburization with CO/H₂ during the synthesis. Namely, the pre-treatment shortened the period of activation (Fig. 1) and retained the steady state activity (Figs. 3 and 4). Therefore, the catalyst once activated by the carburization with CO/He showed immediately the steady-state formation of hydrocarbons, as indicated by the curves 4 and 5 in Figs. 3 and 4.

Niemantsverdriet et al. reported extensive and detailed work (15) concerning to behavior of carbon on and in iron catalysts and proposed the elegant mechanism of "Competition Model" (25). In this mechanism the surface carbon is involved in three reactions: (1) reaction with iron to carbide, (2) reaction with surface hydrogen to the intermediates and (3) reaction with carbon to inactive carbon (catalyst poison). Reaction (2) has been discussed already elsewhere² and reaction (3) is not very important in the present work because of good stability of the commercial iron catalyst used (Fig. 1). Reaction (1) is so fast (25) that most of the carbon atoms are consumed by the carburization of bulk phase in an early stage of the synthesis. Iron catalysts, therefore, require some periods for activation in the formation of hydrocarbons.

As shown in Fig. 4, CO desorbed in two ranges of temperature from the carburized catalyst (200–400 and above 600°C), while it desorbed in one temperature range from the fresh catalyst (400–550°C). Zagli et al. (26) found the high temperature CO desorption in supported nickel catalysts and suggested that this desorption was due to carbon-oxygen recombination. Galszka et al. (27) concluded that the sources of carbon and oxygen for the second CO desorption were carbon formed by the CO decomposition and oxygen of catalyst support, respectively. From these suggestions, the high temperature CO desorption from the carburized fused iron catalyst is presumably due to the recombination between carbidic carbon and oxygen formed during the reactions, since such desorption was completely absent in the case of the fresh catalyst. The amount of CO desorption increased from 38 to 46 or 69 $\mu\text{mol g}^{-1}$ by the carburization with CO/He or CO/H₂, respectively, as shown in Table 1. This difference is considered to come from the different degree of carburization (26.2 and 49.0 mg g^{-1} for with CO/He and with CO/H₂, respectively), since both catalysts showed the similar X-ray diffraction pattern and the similar TPD spectra (Figs. 3 and 4).

With respect to the reason why iron carbide is active whereas metallic iron is not, therefore, the author takes up the position that carbidic carbon weakens the CO-Fe interaction and raises the surface concentration of more weakly bound CO species which are considered to be available for the catalysis (28).

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