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THE CATALYTIC EFFECT OF CARBIDE FORMATION DURING FISCHER-TROPSCH SYNTHESIS

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Fischer-Tropsch reaction on a fused iron catalyst has been investigated in both isothermal (250 °C) and temperature programmed (25 - 800 °C) experiments. With the increase in weight of the catalyst during the reaction, the period of catalyst activation decreased and the rate of hydrocarbon formation increased proportionally. Carburization during the reaction was observed to weaken the interaction between CO and Fe and to increase the amount of more weakly held carbon species which are considered to be available for the catalysis.

The state of Fischer-Tropsch catalysts apparently changes under reaction conditions. Most of kinetic works have been analyzed by the idea that catalysts act in metal states. Recent researches have been concentrated on questions concerning to the interactions between carbon species and metals. However, it has been known that transition metal catalysts form carbides during reaction. Although the role of carbides in the catalysis is still obscure, there is no doubt that the rate of reaction is closely related to the carbide formation.1),2),3) It is not the present purpose to engage in details of the reaction mechanism, rather the author wishes to investigate qualitatively catalytic roles of carbidic carbon which has been considered to be the reaction intermediate in some reports.

Fischer-Tropsch reaction over a fused iron catalyst was simultaneously followed by temperature programmed gravimetry (TG, Ulvac TGD-3000H), gas chromatography (GC, Poropak Q column) and mass spectrometry (MS, Ulvac MSQ-150) with six channels programmer. The iron catalyst used in this work was CCI fused magnetite with the composition : Fe_3O_4, 96.5; Al_2O_3, 2.5; K_2O, 0.6 and SiO_2, 0.4 %. Prior to the reaction, the catalyst was reduced by ultra high pure hydrogen for a period of 30 hours at 550 °C. The specific surface area of the reduced catalyst was determined to be 13.0 m^2/g by the BET method. The reactant mixture used in this work was 10 % CO in H_2. The computation of reaction rates was simplified by the method described elsewhere.1)

After the catalyst was reduced in H_2, the reactor was cooled down to room temperature and then evacuated for one hour prior to exposure to the reactant mixture. When a constant flow of the stream of reactant was obtained, the catalyst was rapidly heated to 250 °C within one minute by an infrared image furnace. The freshly reduced catalyst showed little activity for the formation of hydrocarbons. The formation

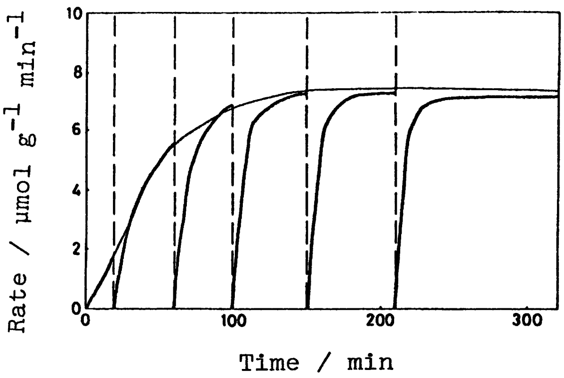

Fig. 1. Formation of CH_4 on the Catalyst with repeated evacuations Vertical broken lines; evacuations for 30 min at room temperature. Thin curve; CH_4 formation in the continuous flow of the reactant.

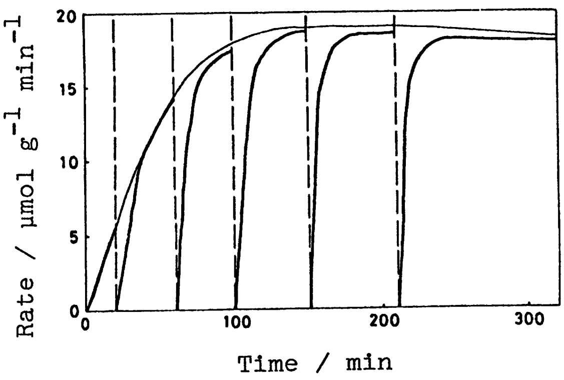

Fig. 2. Formation of C_2H_6 on the catalyst with repeated evacuations. Vertical broken lines; evacuations for 30 min at room temperature. Thin curve; C_2H_6 formation in the continuous flow of the reactant.

rates of CH_4 and C_2H_6 increased gradually with time on stream until a steady state was obtained, as indicated by thin curves in Figs. 1 and 2, respectively. Other higher hydrocarbons, such as propane and butane, were formed in the similar manner. On the other hand, no appreciable period of activation was observed in the formation of H_2O and CO_2. The rates of the H_2O and CO_2 formation decreased slowly with time on stream.

The nature of the period of activation in the formation of hydrocarbons was examined as follows. At 20 minutes after the reaction started, the catalyst was cooled to room temperature and evacuated for 30 minutes to remove the reactants and the intermediates from the surface. After the evacuation the catalyst was rapidly heated to 250 °C in the stream of the reactant. The similar evacuation was carried out repeatedly at 60, 100, 150 and 210 minutes after the reaction started. The results are shown by thick curves in Figs. 1 and 2. After each evacuation, the rates of hydrocarbon formation increased rapidly to the level of the continuous experiment shown by thin curves. These results are considered to suggest that the original iron itself has poor activity for the formation of hydrocarbons and gradually changes its state to an active form during the course of reaction. Since the reaction intermediate has been found to be quite unstable to a helium treatment,1) the evacuation for 30 minutes seems to be enough to remove the intermediate from the surface. When the the catalyst was once activated, therefore, its activity was retained almost completely, as indicated in Figs. 1 and 2.

The weight of the catalyst increased gradually as the carburization proceeded in the course of reaction. Figure 3 shows the relation between the weight increase of the catalyst measured by TG and the rates of hydrocarbon formation. The rates of CH_4 and C_2H_6 formation increased proportionally with the increase in catalyst weight up to 50 mgC/gFe and attained stationary values. Raupp and Delgass3) reported that promoted iron catalysts formed χ-carbide ($Fe_{2.5}C$) during reaction. Amelse, Butt and Swartz2) found the formation of έ-carbide ($Fe_{2.2}C$) in the similar conditions.

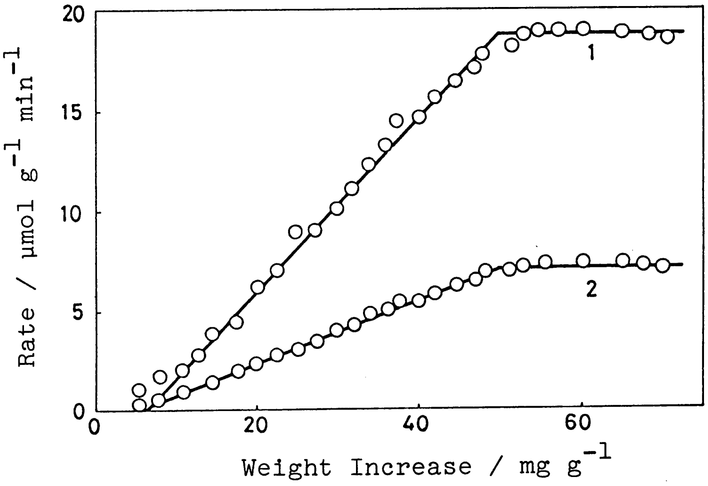

Fig. 3. Effect of carburization on the catalytic activity. 1, CH_4; 2, C_2H_6.

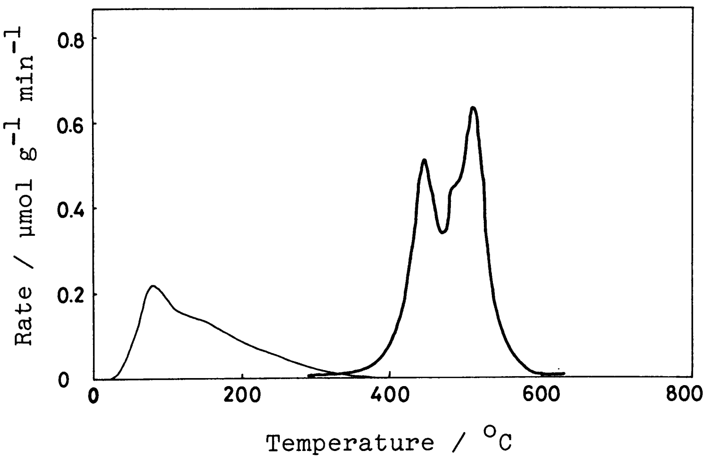

Fig. 4. Programmed desorption spectra of CO and CO_2 for CO adsorption on the fresh catalyst. Thick curve, CO; Thin curve, CO_2.

Therefore, the weight increase of 50 mgC/gFe is smaller than the expected amount of carbon when iron phase is fully carburized to yield χ-carbide (86 mgC/gFe) or ε'-carbide (98 mgC/gFe). However, they also reported that carburization of bulk phases incompleted even after 6 hours of the reaction. Since the carburization is considered to proceed from the surface into the bulk by diffusion of carbon, the available surface for the catalysis has presumably carburized enough by an amount of carbon which is much smaller than the expected one. There is no question that the weight increase can not be attributed only to the carbide formation during reaction. The discrepancy of the two lines from the origin in Fig. 3 may be due to surface oxygen formed by the dissociative adsorption of CO in the early stage of the reaction.[1),4)] Since no significant difference in the weight increase for the activation was observed between CH_4 and C_2H_6 formation, it is suggested that both reactions take place on the similar sites of the catalyst. From these points of view, it is speculated that the active surface for hydrocarbon formation is not iron itself but carbide produced during reaction.

It has been confirmed in many works that the order of reaction in Fischer-Tropsch synthesis are 1 and 0 (or minus), respectively, for H_2 and CO. This may suggest the strong adsorption of CO compared to H_2. Vannice reported that the rates of hydrocarbon formation increased with the increase in the surface concentration of more weakly bound CO species.[5)] Measurements of temperature programmed desorption (TPD) were carried out to provide informations about the difference between the fresh catalyst (α-iron) and the utilized catalyst (iron carbide). Figure 4 shows TPD spectra of CO adsorbed on the fresh catalyst. The evacuated catalyst was treated with pure CO for one hour at room temperature and then evacuated again for three hours to remove physically adsorbed CO. TPD was examined at the rate of 2 °C/min in a stream of helium. As indicated in

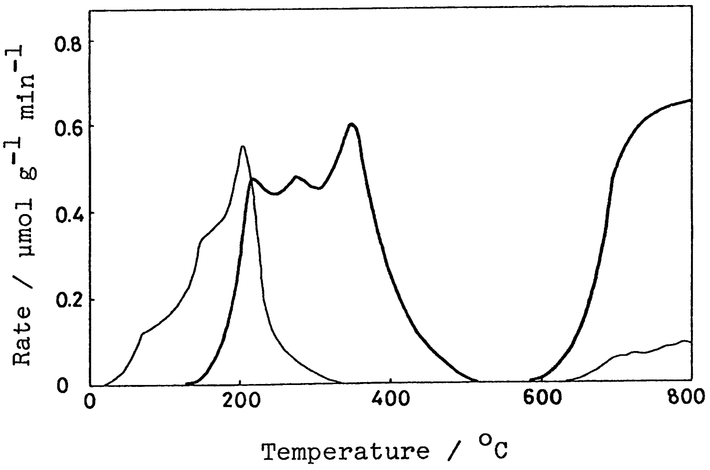

Fig. 5. Programmed desorption spectra of CO and CO_2 for CO adsorption on the utilized catalyst. Thick curve, CO; thin curve, CO_2.

Fig. 4, CO desorbed in three peaks from 400 to 600 ^{o}C, whereas CO_2 desorbed in a single broad peak at the initial stage of TPD. Since the amounts of CO and CO_2 desorbed are estimated to be 19.5 and 9.2 μmol/g, respectively, almost half the adsorbed CO decomposed to yield CO_2 and surface carbon.

TPD spectra of CO adsorbed on the utilized catalyst were quite different from those on the fresh catalyst, as shown in Fig. 5. After the treatment by the CO/H_2 mixture for 100 minutes at 250 ^{o}C, the catalyst was evacuated for one hour and CO was saturated at room temperature in the similar way. The saturated catalyst was again evacuated for three hours and then TPD was examined at heating rate of 2 ^{o}C/min. As seen in Fig. 5, the CO desorption consisted of three peaks from 200 to 500 ^{o}C and of a broad peak above 600 ^{o}C which was not observed in the case of the fresh catalyst. Carbon dioxide desorbed in large peaks near 200 ^{o}C and in a small peak above 600 ^{o}C. The amounts of CO and CO_2 desorption in the region of lower temperatures are 34.4 and 17.3 μmol/g, respectively. The high temperature CO and CO_2 desorptions may be due to the carbon formed during reaction.

Thus, the role of the carbide formation during reaction is considered to weaken the interaction between CO and the surface and to increase the surface concentration of more weakly bound carbon species which are considered to be available for the catalysis. Further experiments are needed to explain the difference in the catalytic action between iron itself and iron carbide. However, the present experiments indicate an impotant role of carbide for the production of active surface during Fischer-Tropsch synthesis.

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