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NOTES

Effects of Preliminary Carburization on the Catalytic Behavior of Fused Iron

It has been well recognized that transition metal catalysts are transformed to their carbides during Fischer–Tropsch synthesis. Roles of the carbides are now the subject of much speculation and experiment. The author has already suggested that the carburization of an iron catalyst plays an important role for the formation of active surface (*1–3*). Similar proposals have been advanced independently by Amelse *et al.* (*4*) and by Raup and Delgass (*5*). It has been a widely spread theory, on the other hand, that carbidic carbon itself is the reaction intermediate in the formation of hydrocarbons. This theory was proposed first by Fischer and Tropsch (*6*) and supported recently by Araki and Ponec (*7*). The objective of the present work is not to engage in details of the reaction mechanism but to confirm if possible the former proposal, by the comparison of catalytic properties between preliminarily carburized iron and metallic iron.

EXPERIMENTAL

Fischer–Tropsch synthesis and temperature-programmed desorption of CO (TPD) were simultaneously followed by temperature-programmed gravimetry, gas chromatography, and mass spectrometry. The detailed experimental procedures and calculation of the rates have been described previously (*1, 2*). The iron catalyst used was a commercial ammonia synthesis catalyst 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 reactions, the magnetite was reduced in H_2 stream for 30 h at 550°C. Measurements of thermal analysis and X-ray diffraction revealed that the magnetite was almost completely converted to α-iron by this reduction. The specific surface area of the reduced iron was determined to be 18.0 m^2g^{-1} by the BET method. Fischer–Tropsch synthesis was examined at 250°C under atmospheric pressure. The precarburization of catalyst was carried out by the decomposition of CO to CO_2 and carbon at 250°C. The reactant mixtures used in the synthesis and in the decomposition were 10.0% CO in H_2 and 10.1% CO in He, respectively, stored in high-pressure cylinders. In most experiments in the present work, the feed rate of the reactant mixture was explored between 7.4 and 7.7 ml min^{-1} on 100 ± 3 mg of magnetite. Prior to TPD measurements, the fresh and precarburized catalysts were treated with pure CO for 1 h at room temperature. After the saturated catalysts were flushed with He for 3 h, they were heated at the rate of 3°C min^{-1} in He stream.

RESULTS

The freshly reduced iron showed little catalytic activity in the formation of hydrocarbons, but activity gradually increased with time on stream until a steady state was obtained in about 150 min after the synthesis started. Rates of the CH_4 and C_2H_6 formations were measured over the catalyst with various degrees of the precarburization. The results are shown in Figs. 1 and 2, in which the rates are plotted against the weight increase of catalyst during the synthesis as well as during the precarburization. The rates of both the CH_4 and C_2H_6 formations over the fresh catalyst (1) increased almost proportionally with the in-

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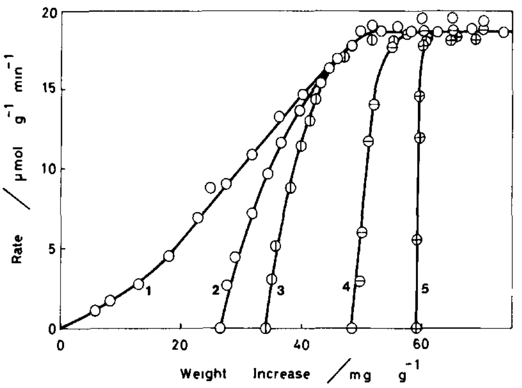

FIG 1 Effects of precarburization on CH_4 formation Period of CO treatment (1) 0, (2) 100, (3) 140, (4) 260, (5) 400 min

crease of catalyst weight up to 50 mg g^{-1} Further increase of the weight showed no virtual effect on the catalytic activity Other higher hydrocarbons, such as C_3H_8 and C_4H_{10}, were formed in a similar manner The weight increases of catalyst during precarburization for 100 (2), 140 (3), 260 (4), and 400 min (5) were 26 2, 33 5, 49 0, and 58 0 mg g^{-1}, respectively The latter values are shown on the abscissae of Figs 1 and 2 The precarburization scarcely affected the steady-state activity of catalyst The period of activation, however, evidently decreased with increase in the degree of precarburization X-Ray analysis of the catalysts treated with CO/H_2 and CO/He showed an identical diffraction pattern in which all predominant peaks corresponded to $Fe_{2\ 5}C$ and α-Fe The existence of other carbides, such as $Fe_{2\ 2}C$ and Fe_2C, was not recognized in the present work, while several kinds of carbide have been found in the case of supported iron catalysts (*8*, *9*)

Figure 3 shows TPD spectra of CO from the two kinds of carbide, together with those from metallic iron (1) These carbides were prepared at 250°C for 100 min by CO/H_2 (2) and CO/He (3) The fresh catalyst desorbed CO in three peaks at 400–600°C The CO desorption from the carburized catalysts, on the other hand, consisted of three peaks at 200–400°C and a broad peak above 600°C No significant difference in shape and temperature range of the desorption was observed between these carbides Figure 4 shows TPD spectra of CO_2 from the three catalysts For the catalysts carburized by CO/H_2 (2) and CO/He (3), CO_2 was desorbed in large peaks near 200°C and small peaks above 600°C The desorption spectra of CO_2 for these carbides bore remarkable resemblances For the fresh catalyst, CO_2 was desorbed in a single broad peak in the initial stage of TPD Temperature-programmed reduction (TPR) was carried out for the catalysts carburized by CO/H_2 and CO/He Heating these carbides in H_2 stream yielded CH_4 in a single sharp peak at 400°C and H_2O in broad peaks at 100–400°C It was indicative that higher hydrocarbons, such as C_2H_6 and C_3H_8, were

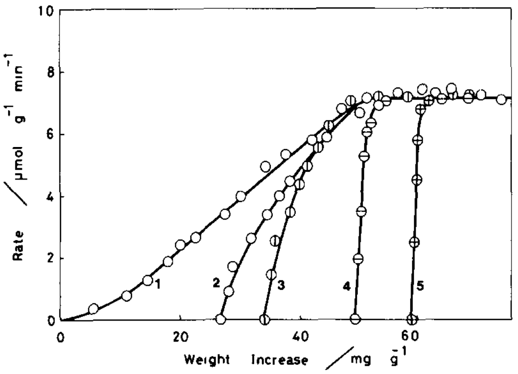

FIG 2 Effects of precarburization on C_2H_6 formation Period of CO treatment (1) 0, (2) 100, (3) 140, (4) 260, (5) 400 min

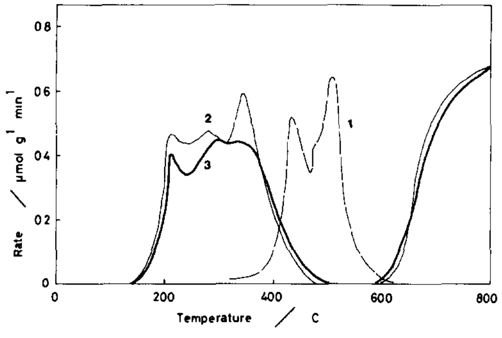

FIG 3 TPD spectra of CO from fresh (1), CO/H_2-treated (2) and CO/He-treated (3) catalysts

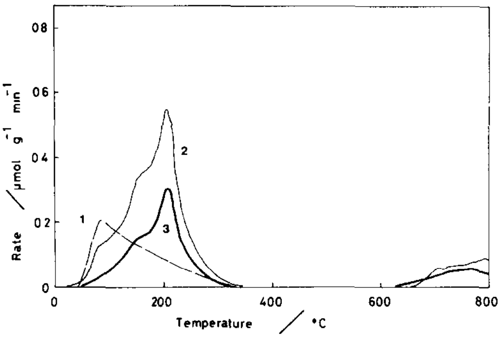

FIG 4 TPD spectra of CO_2 from fresh (1) CO/H_2-treated (2) and CO/He-treated (3) catalysts

completely absent in the TPR products of both carbides

DISCUSSION

Rates of hydrocarbon formation increased with increase of catalyst weight in the course of synthesis, although metallic iron showed little catalytic activity (Figs 1 and 2) The activity was retained toward evacuation of the catalyst (*2*) The carburized catalysts formed CH_4 as the only hydrocarbon product in TPR experiments This carbon species is supposed to be carbidic carbon of the bulk phase [hydrogenated at 400°C] which is much more inactive than the reaction intermediates [hydrogenated easily at 250°C (*1*)] In the catalytic activities (Figs 1 and 2) and the adsorptive properties (Figs 3 and 4), furthermore, no significant differences were observed between the carbides formed by the CO/H_2 and CO/He treatments From these points of view, it is postulated that carburization during the synthesis mainly contributes not to the formation of reaction intermediates but to the development of active surface available for the catalysis

According to the "Competition Model" proposed by Niemantsverdriet and van der Kraan (*10*), carbon species on the surface are involved in three reactions (1) reaction with Fe to carbides, (2) reaction with H to intermediates and (3) reaction with C to inactive carbon Reaction (2) has been discussed already elsewhere (*1*) and reaction (3) is not very important in the present work because of the good stability of the commercial catalyst used Reaction (1) is considered to occur (*11*) so fast that most of the carbon atoms are consumed by the carburization of bulk phase in an early stage of the synthesis The weight increase required for the maximum rate was 50 mg g^{-1} (Figs 1 and 2) This value is smaller than that expected when the iron phase of the catalyst is fully carburized to yield $Fe_{2\ 5}C$ (86 mg g^{-1}), $Fe_{2\ 2}C$ (98 mg g^{-1}), or Fe_2C (107 mg g^{-1}), even if the existence of surface oxygen could be disregarded The surface available for the catalysis, however, is considered to have been carburized enough by an amount of carbon which is much smaller than these values, since the carburization proceeds from the surface into the bulk by diffusion (*12, 13*)

As shown in Fig 3, CO was desorbed in two ranges of temperature from the carburized catalysts (200–400 and above 600°C), while it was desorbed in one range from the fresh catalyst (400–500°C) The high temperature desorption of CO from the carburized catalysts is presumably due to the recombination between carbidic carbon and oxygen formed during the reactions (*14, 15*), since such desorption was absent in the case of the fresh catalyst In TPD spectra (Figs 3 and 4), accumulated amounts of CO desorption from the fresh, CO/H_2- and CO/He-treated catalysts are estimated to be 19 5, 34 4, and 30 0 μmol g^{-1}, respectively, and those of CO_2 desorption are 9 2, 17 3, and 7 8 μmol g^{-1}, respectively The high-temperature desorptions are excluded from the estimation Thus, if it can be assumed that CO_2 is formed only by the reaction $2CO = C + CO_2$, the total amounts of CO adsorption on the fresh, CO/H_2- and CO/He-treated catalysts are 38, 69, and 46 mol g^{-1}, respectively With respect to the reason why iron carbide is active whereas metallic iron is not, therefore, it is speculated that carbidic carbon weakens the CO–Fe interaction and increases the surface concentration of more weakly bound CO species which are considered to be available for the catalysis (*16*)

Further detailed experiments are needed to determine fully the role of carbon species for iron catalysts In a study of Fe on carbon catalyst (*17*) Jung *et al* have clearly explained that the excellent activity maintenance is a result of formation of the transition iron carbides and their stabilization on the carbon support Furthermore, the formation of available catalyst surface does not always depend on the carburization of surface iron Nitride (*18*) and oxide (*19*) catalysts had higher activity and better activity maintenance in comparison with reduced iron Reymond *et al* (*20*) showed that surface carbon species active in the synthesis were formed more abundantly on Fe_3O_4 than α-Fe

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