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On the Time-Dependent Behavior of Iron Catalysts in Fischer–Tropsch Synthesis

Among the metals that display activity for Fischer–Tropsch synthesis, iron seems to occupy a special place. Its activity in the synthesis is initially low and increases slowly to a maximum, while simultaneously iron carbides are formed (*1–3*) (Fig. 1a,b). Cobalt and nickel, on the other hand (Fig. 1c), are active for the hydrocarbon formation from the beginning of the process and although carbides of these metals exist, no bulk carbides are formed during the synthesis. A model aiming to explain the behavior of iron in the Fischer–Tropsch (FT) process should also make clear why iron behaves differently from the other FT catalysts. Three explanations concerning iron during FT synthesis have been proposed in the literature. In this note we will discuss some experiments which in our opinion can discriminate between these explanations.

First we will give a brief survey of the explanations, which for easy reference will be denoted as the "carbide model," the "competition model," and the "slow activation model," respectively.

In the *carbide model* iron is not active for FT synthesis and the real catalyst has an iron carbide bulk structure with active sites on its surface. This explanation is favoured by many authors (*1, 2, 4*), in particular by Raupp and Delgass (*2*). In a very elegant *in situ* Mössbauer experiment they noticed that the FT activity increased almost linearly with the extent of carbidation. They suggest that this relationship is causal in the sense that the state of the bulk controls the number of active sites at the catalyst surface.

In the *competition model* (*3*) iron atoms at the surface of the catalyst are seen as the active sites. After adsorption and dissociation of CO and H_2 three reactions involving the surface carbidic C* are possible:

$$C^* + \text{iron} \rightarrow \text{carbides}, \qquad \text{(i)}$$

$$C^* + xH^* \rightarrow CH_x^*, \qquad \text{(ii)}$$

$$C^* + yC^* \rightarrow \text{inactive carbon}. \qquad \text{(iii)}$$

Reaction (i) implies bulk diffusion of carbon into metallic iron, and this process is known to occur very fast (E_a = 10–16 kcal/mole). So in an early stage of the synthesis most of the carbon atoms are consumed by the carbidation reaction (i). When the bulk of the catalyst becomes more and more carbided, progressively more C* remains at the surface and becomes available for either hydrocarbon synthesis (ii) or deactivation (iii). So the rate of reaction (ii) goes through a maximum. The reactions compete as long as CO dissociation is slower than carbidation.

In the *slow activation model* (*3*) CO adsorption and dissociation are faster than all subsequent reactions, so that sufficient carbon is present on the surface to fulfill the demands of both bulk carbidation and hydrocarbon synthesis. Hence these processes are autonomous. Hydrogenation is believed to occur at surface complexes consisting of iron, carbon, and hydrogen atoms in a certain configuration. The FT activity is initially low because these complexes are thought to be formed at a low rate. In other words, the iron surface is slowly activated.

The three models have in common that deactivation results from the blocking of catalytically active sites by inactive carbon and possibly also by hydrocarbons with high boiling points.

All three models can account for the presence of at least three forms of carbon in the active iron catalyst, namely, bulk carbidic, inactive and surface carbidic carbon.

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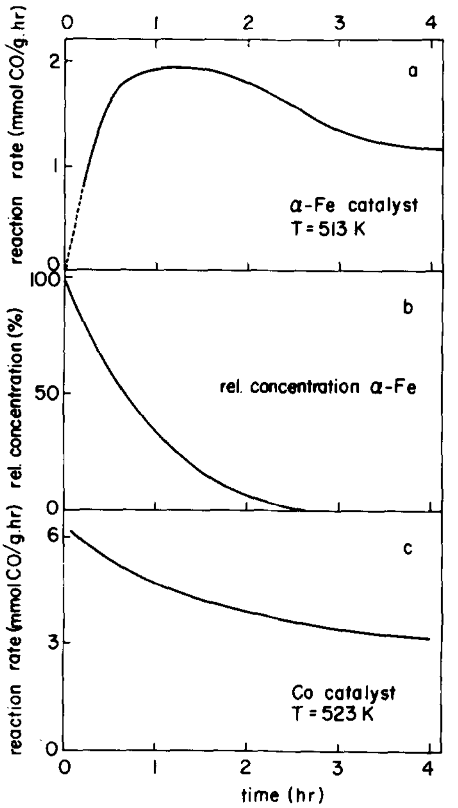

FIG. 1. Fischer–Tropsch reaction rates over (a) single-phase iron (*3*) and (c) single-phase cobalt (*15*) (H_2 : CO : He = 1 : 1 : 3, 1 atm), and (b) relative concentration of α-Fe during the synthesis as determined with Mössbauer spectroscopy (*3*).

The presence of bulk-carbidic and inactive or free carbon in iron FT catalysts has already been known for more than 30 years (*5*), but knowledge about the surface-carbidic carbon has been obtained only recently with surface sensitive techniques (*6*).

Although the models are obviously different, each of them can also account for the results in Fig. 1a,b. We will now cite some experiments which in our opinion can discriminate between the three explanations.

PRECARBIDED CATALYST

Matsumoto and Bennett (*7*) reported extensive and very detailed FT experiments at 250°C with a commercial fused iron catalyst. When a carbided catalyst at steady-state activity is subjected to pure hydrogen, the immediate formation of a large amount of methane is observed, the rate of which decreases rapidly to a "pseudo-constant" level. The authors interpret this as the rapid hydrogenation of surface carbon, intermediate in the FT synthesis, followed by the much slower hydrogenation of bulk carbides when the active carbon phase has disappeared. Raupp and Delgass (*2*) give a similar interpretation for their hydrogenation experiments with fully carbided iron catalysts.

In this way Matsumoto and Bennett (*7*) prepared a catalyst with a carbided bulk structure but a clean iron surface. This catalyst is immediately active in the FT synthesis and its activity shows a temporary overshoot compared to the steady-state activity in the standard experiment.

The result that a clean iron surface with an underlying bulk carbidic structure is initially active in FT synthesis is evidently in agreement with the carbide model since it will only take a very short time before the surface will be carbided. Also the competition model allows for a satisfactory explanation of this experiment. In this model the clean iron surface is active for FT synthesis and since the bulk of the catalyst has already been carbided all C* deposited from the synthesis gas remains at the surface to form either hydrocarbons or inactive carbon. However, we believe that this experiment does not support the slow activation model, since on a clean iron surface the necessary iron carbon complexes are thought to be formed at a low rate and it is hard to imagine why the presence of an underlying carbide structure should have such a profound effect on the formation rate of these complexes.

PREOXIDIZED CATALYST

Dwyer and Somorjai (*8*) investigated the hydrogenation of CO over polycrystalline iron foils at 300°C and found the commonly observed activity pattern of iron. They oxidized one of the foils and observed a tenfold increase in initial methanation rate compared to reduced iron foils. With Auger spectroscopy it is seen that about 25 min of synthesis are needed to remove all oxygen from the upper layers of the foil. During that time the preoxidized foil has already produced five times more methane than a reduced foil. Dwyer and Somorjai (*8*) conclude that in the reducing atmosphere of CO + H_2 highly active iron atoms or clusters are formed at the surface and that these iron sites probably are the active centers for FT synthesis.

The carbide model cannot explain this experiment. Irrespective of whether the reduced or the unreduced iron atoms in the oxidized foil catalyze the rapid hydrogenation, the active surface is certainly not the result of a bulk carbidic structure underneath it. As it is hard to understand why the necessary iron–carbon complexes should be formed rapidly on freshly reduced iron atoms on an underlying oxide and only slowly on metallic iron itself, we believe that the slow activation model also fails here. The experiment is consistent with the competition model. Here the freshly reduced iron atoms or clusters are active for the FT synthesis. Since diffusion of carbon into iron oxide does not take place and reduction of iron oxide at 300°C occurs only slowly, almost all surface carbidic carbon is available for the FT reaction and a high activity is expected.

IRON-RUTHENIUM ALLOY CATALYST

Ott, Fleisch, and Delgass (*9, 10*) reported FT experiments over FeRu alloys in a composition range where bulk carbides do not exist. Strong surface enrichment of iron occurs in these alloy catalysts. When used in FT synthesis at 573 and 617 K the catalysts show a high initial activity, which is found to increase with increasing iron content. This high initial activity, however, is followed by rapid deactivation. No carbides are formed during the synthesis.

We believe that this experiment clearly shows that iron in FeRu alloys can be active for FT synthesis without the presence of a bulk carbide structure in the catalyst; hence the experiment is not in agreement with the carbide model. Since the iron at the alloy catalyst surface shows a high initial activity, the slow activation model also fails here. The FeRu experiments can, however, be easily understood in terms of the competition model. Here the iron atoms at the surface are active sites and carbon atoms deposited at these sites are available for FT synthesis and deactivation, since no bulk carbidation occurs.

Recently it was found (*11*) that the iron nitride Fe_4N is immediately active for Fischer–Tropsch synthesis at 240°C, while the conversion of Fe_4N into iron carbonitrides and carbides occurs on a much longer time scale, as was seen in Mössbauer experiments. Also, in this case a correlation between a high initial activity and a low rate of carbon diffusion into the bulk of the catalyst is clearly observed, consistent with the competition model.

DISCUSSION

We believe that the failure of the slow activation model and the carbide model in explaining respectively four and three of the four experiments referred to above, forms sufficient evidence to reject these models. The general tendency of the experiments is that when diffusion of carbon into the catalyst can be prohibited the FT rate starts at an initially high value. This is in agreement with the concept that iron itself is active for FT synthesis and that a competition between carbidation (reaction (i)), hydrogenation of surface carbon (reaction (ii)), and deactivation (reaction (iii)) governs the rate of the FT synthesis, i.e., that the competition model, operates.

The apparent linear relationship that Raupp and Delgass (*2*) found between extent of carburization and FT activity has not been found by Amelse *et al.* (*1*) and Niemantsverdriet *et al.* (*3*). They observed that their iron catalyst was at maximum activity significantly before all iron had been converted into carbides. Vannice (*12*) reports that the CO + H_2 reaction is near first order in hydrogen and close to zero order in CO. These reaction orders are valid in a range of experimental conditions which include those of the three mentioned investigations (*1–3*). So the FT activity (ii) will be strongly dependent upon the hydrogen partial pressure. Furthermore, the carbidation rate and hence the extent of carbidation depend on the particle size, such that small particles carbide faster than larger particles (*13*). It is conceivable that combinations of particle size and H_2/CO ratio exist that may result in a more or less parallel course of FT activity and extent of carburization, while other combinations do not.

In order to explain why iron differs from cobalt and nickel in time dependent FT behavior we will consider the activation energies for carbon diffusion (*14*), which are 10.5–16.5 kcal/mole for α-Fe, 33.0–34.8 kcal/mole for Ni and 34.7 kcal/mole for Co, and the activation energies for the FT reaction (*12*), 21.3 ± 0.9 kcal/mole for α-Fe, 25.0 ± 1.2 kcal/mole for Ni and 27.0 ± 4.4 kcal/mole for Co. Since the exponential factors for both groups of reactions are equal within a factor of 40, a comparison of reaction rates based on activation energies alone is justified.

In the case of iron the carbidation rate is higher than the FT rate (*3*), which results in carbon deficiency in the early stage of the synthesis. In the case of cobalt and nickel the rates of carbon diffusion into the catalyst are slower than in iron by a factor of 10^5. So with cobalt and nickel catalysts the FT reaction rate will be much larger than the carbidation rate. Hence the difference between iron and the other FT catalysts can be understood in terms of the different rates of carbon diffusion into the metals.

We therefore believe that the competition model satisfies the requirements formulated in the introduction of this paper and that it accounts satisfactorily for the time-dependent behavior of iron-containing catalysts during Fischer–Tropsch synthesis.

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