FISCHER-TROPSCH PRINCIPLES OF CO-HYDROGENATION ON IRON CATALYSTS

Hans Schulz

University of Karlsruhe
Engler-Bunte-Institute
76131 Karlsruhe, Germany

Introduction

The products of Fischer-Tropsch synthesis on iron catalysts can be composed very similarly as those obtained on cobalt catalysts. This similarity requires a common principle of their formation. But amazingly, FT-synthesis on iron catalysts differs in many regards when compared with FT-synthesis on cobalt:

(1) With cobalt increasing the reaction temperature from e.g. 210 to 350 °C, changes the selectivity to methane as for being the dominant product (e.g. 90 C %). With iron even at 350 °C the methane selectivity can remain low (e.g. 7 C %): The FT-regime is stable over a wide range of temperature.

(2) Increasing the H_2/CO-ratio, respectively reducing the CO partial pressure, changes the FT-selectivity to almost pure methane (at low CO partial) whereas with iron, even when reducing the CO-partial pressure to very low values, the selectivity is merely effected. This means that the FT-regime with cobalt can only exist at sufficiently high CO-partial pressure as in contrast to iron.

(3) Increasing H_2O-partial pressure does positively affect FT-synthesis on cobalt; lowering methane selectivity, increasing chain growth probability, increasing syngas conversion (at some circumstances high H_2O-partial pressure can deactivate the catalyst). With iron, H_2O does inhibit the FT-reaction and restricts the degree of conversion.

(4) Alkali is a very efficient and essential promotor for FT-synthesis on iron, having strong effects on reaction rate and selectivity. With cobalt, no or only minor effects of alkali are noticed.

(5) The water-gas-shift reaction and its reverse generally perform fast on (alkalized) iron catalysts but are not (or only poorly) observed with cobalt catalysts.

(6) The byproducts of FT-synthesis, respectively the minor reactions performing additionally to the main stream of non-trivial surface polymerization, are significantly different with iron- as compared with cobalt catalysts. With cobalt, in contrast to iron, secondary olefin reactions of hydrogenation, isomerization and incorporation occur. Also relations to organic complex catalysis (olefin-hydroformylation, olefin-polymerization and carbene reactions) are noticed in contrast to the performance on iron catalysts.

(7) With both the catalyst metals, processes of self-organization and restructuring of the catalyst occur but they are different in principle with iron and with cobalt. With cobalt the interaction of the cobalt metal with the reactants concerns segregation of the surface. With iron it concerns reaction with carbon, being formed from CO-dissociation to produce iron carbide phases and structured or amorphous carbon phases in addition to further compositional catalyst changes.

In this paper, specifically, the processes of self-organization of the Fischer-Tropsch regime with (alkalized) iron as the catalyst are regarded, as in contrast to the behavior of cobalt catalysts.

Results and Discussion

It is seen in Fig. 1 that the Fischer-Tropsch activity - a measure hereof is the yield of FT-products (Y_{FT}) - initially ($t_{exp.}$ ca. 10 min) is about zero in all the three cases. The precipitated catalysts had been reduced with hydrogen and - generalizing - about half of the iron was in the state of metallic iron and the other half in the state of magnetide in the beginning. So it is concluded that iron in its metallic form exhibits "no" Fischer-Tropsch activity. This is in contrast to e.g. cobalt or ruthenium where essentially the metal is the active phase for FT-synthesis.

The catalyst activity develops with time in about 5 episodes, respectively, kinetic regimes. Episode I relates to the very first contact of the synthesis gas with the catalyst when it replaces the inert gas in the reactor and chromatographic effects and reactor residence-time-behavior overlap with the conversion of reactants.

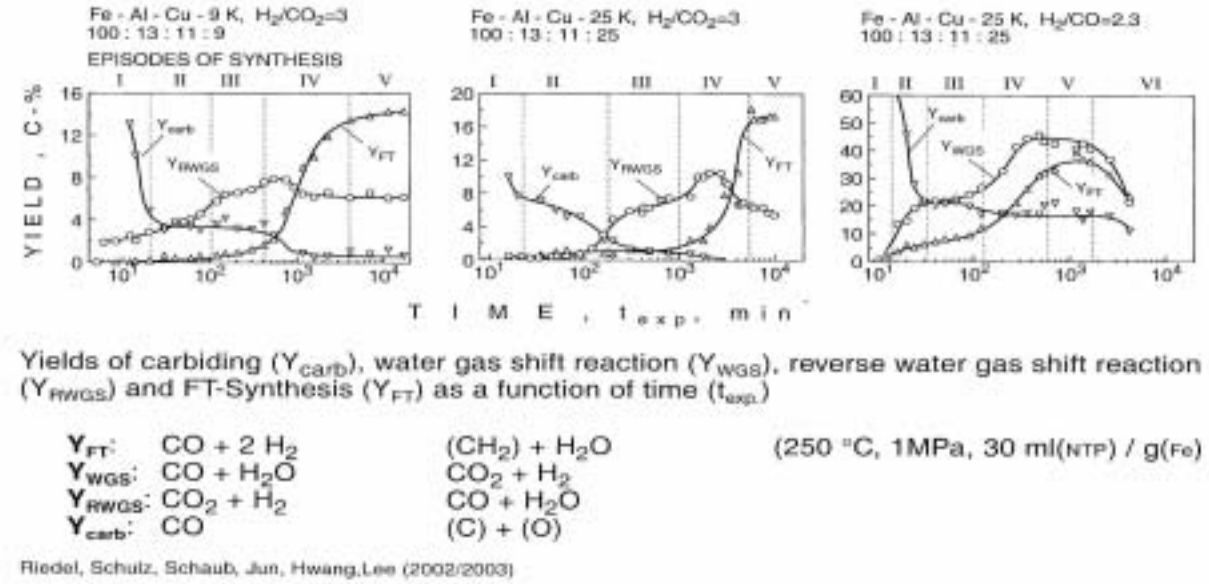


Figure 1. Initial episodes of FT-synthesis with iron as the catalyst.

In Episode II, the main process is the deposition of carbon (Y_{carb}) on the iron catalyst. The carbon yield increases to about 20 C % with the (H_2/CO = 2,3)-syngas (Fig. 1, right). With the (H_2/CO_2 = 3)-syngas the carbon yield is less excessive - e.g. 4-6 C % in Episode II (see Fig. 1, middle and left). Here with no CO but only CO_2 in the syngas, the carbon can only be formed as much as CO has been formed by the reverse water-gas-shift reaction. It is seen that also the water-gas-shift activity develops in-situ, prior to FT-activity. But even when in Episode III more CO has been formed from CO_2 plus H_2 (Y_{RWGS}), only marginal FT-activity is noticed (Fig. 1, left and middle). Then, in Episode IV after a number of hours on stream, the Fischer-Tropsch reaction sets in. Obviously, a distinct extent of iron carbiding is necessary for the catalyst to exhibit FT-activity. With the $3H_2/CO_2$-syngas this process of carbiding is slower as compared with the $2H_2/CO$-syngas.

Episode V is the steady-state of FT-synthesis. With the ($2H_2/CO$)-syngas a deactivation in Episode VI is noticed as caused by ongoing carbon formation due to high catalyst alkalization which is favorable at very low CO-partial pressure but too high for a CO-rich syngas.

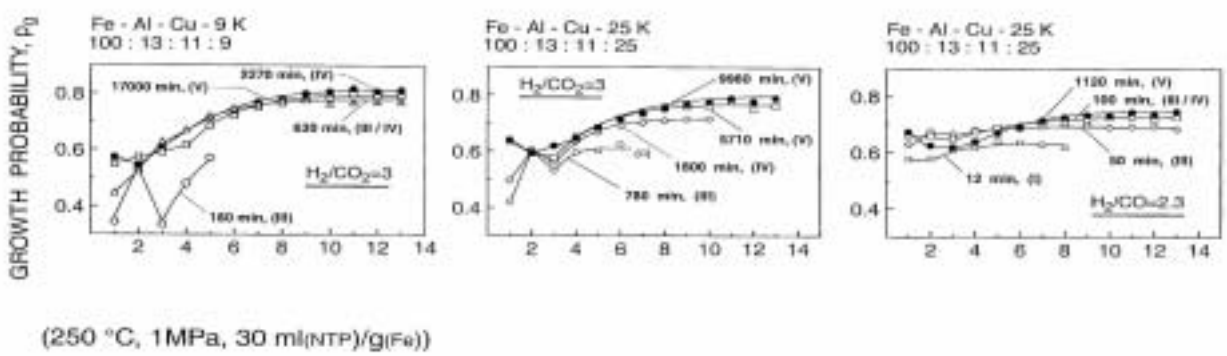
In Fig. 2 the chain prolongation probability as a function of carbon number is presented for different times on stream and for the same three experiments as in Fig. 1. The result is very remarkable (and in complete contrast to what would be observed with cobalt catalysts). In dependence of time-on-stream only for the initial episodes (up to Episode III) when FT-yields are very low, the curve of growth probability is markedly affected. But during Episode IV when the FT-regime is being established as the FT-yield increases substantially, the curve shape changes only marginally. And even when comparing the steady-state curves for the three experiments the differences are small.

The surprising conclusion is that the FT-chemistry remains much the same, during establishing the FT-regime and even with both the synthesis gases $3H_2/CO_2$ and $2,3H_2/CO$.

It follows that increasing FT-activity here means an increase of the number of active sites, however, their nature being the same. And as the chemistry (selectivity) is invariant against the partial pressures, specifically of CO, that the sites are not dynamic in nature (in contrast to FT with cobalt).

When now searching for the common FT-principle with iron and cobalt catalysts, it should be a kinetic law, defined more by the sort of involved species than the catalyst composition (iron or cobalt). It is proposed to concern the frustration of the desorption reactions (for paraffins and olefins) thus allowing for the alternative reaction of adding C_1-species to the adsorbed chain.

In a complementary study of catalyst composition (and structure) as a function of time by XRD, Moessbauer spectroscopy, XPS it was observed that the FT-activity started to develop in correlation to the conversion of the alpha-iron-phase to a Fe_5C_2-carbide-phase. The carbide-phase is therefore regarded to possess the FT-active sites under reaction conditions and these sites appear to be very stable entities.



At steady state (Episode 5), nearly the same carbon number dependence of growth probability is obtained in all the 3 cases,"no" extra-methane formation is noticed

With CO_2, olefin readsorption is more pronounced than with CO

Reactions on the FT-sites are very independent on partial pressures of CO andCO_2, on degree of conversion and on catalyst activity (degree of carbiding)

Figure 2. Chain growth as a function of time ($t_{exp.}$)