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Spatial constraints and frustrated reactions in Fischer–Tropsch synthesis

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Abstract

Recent results about Fischer–Tropsch (FT)-synthesis, obtained with newly available research tools, allow for an advanced understanding of the unique regime of Fischer–Tropsch catalysis, where CO and hydrogen enter and a hydrocarbon liquid mixture exits the reactor. Obviously, a multistep conversion is taking place on the catalyst surface. Rules, which govern the regime, become visible and among these spatial constraints and frustrated reactions—indicating specific reaction barriers—apparently dominate the system. Of course, an appropriate theory would require knowledge about both the active sites and the reaction intermediates Substantial evidence about both these aspects is becoming available.

Keywords: Fischer–Tropsch synthesis; Cobalt catalysts; Formation of the FT-regime; Time resolved selectivity; Active sites disproportionation; Spatial constraints; Frustrated reactions

Active sites of Fischer–Tropsch (FT)-synthesis on cobalt, ruthenium and nickel, evidently, are of similar kind. Similarities of kinetic rules and details in selectivity prevail with these catalysts. The reaction conditions of FT-synthesis are similar to those for allowing the formation of metal carbonyls by reaction of the catalyst metals with carbon monoxide [1]. The FT-reaction takes place on these catalysts in their metallic state and is possible without promoters [2,3]. The initial activity of the catalyst metals is low and the intrinsic FT-feature, the polymerization nature of the conversion, is initially not fully developed (low initial chain growth probability). Then activity for CO consumption and selectivity for chain prolongation increases slowly, but significantly (by a factor of 2–3) with time, indicating a catalyst restructuring, or a "catalyst construction", under reaction conditions to create the Fischer–Tropsch domain of catalysis [4–6]. Surface roughening of cobalt metal crystal planes through FT-synthesis has correspondingly been observed by STEM imaging [3].

Considering this self-organization of the FT-regime, the related catalyst surface restructuring is now visualized from a chemical perspective: two opposite trends are to be taken into account. As for lowering the specific surface energy, surface annealing and sintering of small particles for crystal growth would be expected. But, as the chemisorption enthalpy of CO is high, the gain of enthalpy through CO-chemisorption over-compensates the enthalpy loss through sintering and as a result, surface planes segregate, allowing for more CO to be adsorbed. But, as metal carbonyl formation is (thermodynamically) restricted under Fischer–Tropsch reaction conditions, this process of segregation will proceed only until an equilibrium state of surface restructuring is established. Thus, the chemisorbed CO is an essential part of the catalytic system. Segregation of the catalyst surface planes does result in disproportionation of active sites:

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disproportionation to sites of lower co-ordination (on top, on peaks) with several free co-ordinates/valences for binding intermediates and species from the fluid phase and sites of higher co-ordination (in holes, in valleys, at kink locations) with less free valencies and a higher propensity for e.g. dual site splitting reactions.

Thus, in the FT-regime we are coping with three sorts of active sites

(1) On-top-sites of low coordination with which their chemistry exhibits similarities to homogeneous complex catalysts.
(2) In-hole-sites of high coordination, suspected of being active for dissociation reactions (specifically of CO).
(3) On-plane-sites of common metallic character, however, due to the ample strong CO-adsorption, these exhibit strongly suppressed activity.

The small-catalyst-metal-crystallite-planes segregation through CO-chemisorption, leading to the equilibrium state, is associated with an increase of the specific surface area without change of the particle size. Furthermore, different degrees of dispersion would be calculated from chemisorption data, as depending on the degree of surface segregation for the same average particle diameter.

It can also be concluded that catalyst regeneration/reactivation procedures by CO/H_2 treatment under appropriate conditions should be capable of surface restructuring to re-obtain an optimal segregated equilibrium state.

FT-reaction intermediates can be divided as belonging to one of the two sorts:

(1) Chemisorbed species.
(2) Reactive compounds in the liquid or gaseous phase.

It is characteristic for FT-catalysis that reaction intermediates are very preferentially chemically attached to the catalyst and numerous consecutive reactions of the attached species can proceed per one desorption reaction. The most intrinsic reaction barrier, inherent for FT-catalysis, is that against desorption of the intermediates. Their repeated reaction with chemisorbed "monomers" for building up even long hydrocarbon chains becomes possible and even dominant. However, the chemisorbed intermediates of Fischer–Tropsch synthesis are not easily identified.

1. The alkyl intermediate

As the principal products of FT-synthesis are terminal linear olefins and linear paraffins, it has convincingly been concluded that they are formed from the same alkyl species by the alternative reactions of β-H-abstraction or α-H-addition [4–6]. As α-olefins readsorb for linear chain growth it is concluded that the alkyl intermediate of FT-synthesis is attached to the catalyst with its terminal C-atom (otherwise methyl-branched chains would be formed by subsequent chain growth). It is also concluded that it is the alkyl species, which is capable for adding the monomer ("nontrivial surface polymerization" in FT-synthesis [7]).

Then the question about the nature of the monomer for chain growth remains. In Fig. 1 the molar radioactivity of products as a function of their carbon number is plotted for an experiment of FT-synthesis with a cobalt catalyst when normal hexadecene: (1) with ^{14}C-labeling at C-atom number one had been co-fed with the synthesis gas [8]. Table 1 presents the distribution of radioactivity in the product. In Fig. 1 we see constant, carbon number independent,

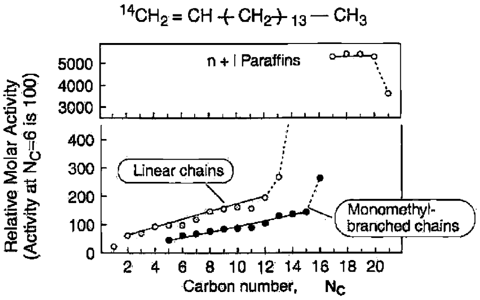

Fig. 1. *n*-Hexene-1 (1-^{14}C) reactions during FT-synthesis on cobalt. Conditions: 100Co–18ThO$_2$–100 Kieseiguhr, 190 °C, H_2/CO = 2, $p = 1$ bar, 75 h^{-1}. CO conversion ~70%, 0.1 vol.% hexadecene ^{14}C in syngas.

Table 1
Selectivity of 1-hexene-^{14}C conversion ($X_{C_{16}H_{32}} = 99.8\%$)

Hydrogenation	80% of ^{14}C (on on-plane-sites)
To products $N_c > 16$	6.3% of ^{14}C[a]
To products $N_cC_2 \sim C_{15}$	10% of ^{14}C
To methane	3.7% of ^{14}C

[a] Proves spatial constraints: the olefin adsorbs at C-atom-1 of the chain.

molar radioactivity of the compounds with carbon numbers higher than 16. This corresponds to the reversible α-olefin adsorption on FT-growth sites. Amazingly, Fig. 1 shows radioactivity of the compounds of lower carbon number than 16 also and here the molar radioactivity increases proportionally with carbon number. This means that for each growth step by one C-atom there is a distinct (same) probability for adding a radioactive carbon and this would be the C_1 from the C_{16} α-olefin. From this result it is concluded that for the chemisorbed alkyl there exists also the possibility of splitting the terminal CH_2 from the chain end (such carbenes are well-known ligands in homogeneous catalysis) and this CH_2 (from alkyl-demethyleneation) can act as monomer for chain growth. As radioactivity of methane is noticed also (Table 1), this methylene has also the possibility for reacting with hydrogen to form methane.

The general conclusions for the Fischer–Tropsch regime with cobalt are

(1) the principal monomer for chain growth is the methylene species;
(2) addition of a CH_2 to alkyls for chain growth is a (at least partially) reversible reaction;
(3) for the outlined alkyl reactions in FT-synthesis on on-top-sites of the catalyst analogies are observed with homogeneous catalysis.

2. The monomer

As discussed earlier, the methylene species (the carbene ligand in complex chemistry) is addressed as major monomer of FT-synthesis. A further species, suspected to react with the alkyl for chain prolongation, would be the CO (see also references [9–11]). However (as known in homogeneous olefin hydroformylation with cobalt carbonyl complexes as catalyst), from the obtained acyl species the oxygen would not be split off and therefore the species do not grow further, but only desorb, forming the minor products of Fischer–Tropsch synthesis: the aldehydes and alcohols.

Another proven minor reaction of chain prolongation would be that of an alkyl with ethene, as in analogy with complex catalyzed ethene oligomerization [8].

Formation of the CH_2-monomer is visualized to perform preferentially on in-hole-sites/in-valley-sites with high propensity for CO-dissociation, the hydrogen atoms for C-atom hydrogenation, being generally present to produce a pool of C_1H_x-species of which the CH_2-species would react with the alkyl for chain growth.

Accumulation of methyl species on spent hydrogenation catalysts has been observed by neutron scattering experiments and conclusions have been made about their high, even deactivating stability [12].

3. Frustrations

Frustration of reactions means their strong suppression in the Fischer–Tropsch regime whereby the real (complex) causalities are not clearly understood.

The most important frustration is that of paraffin formation by associative desorption of alkyl with hydrogen. Fig. 2 gives an example.

As presented in Fig. 2, also desorption as olefin is suppressed, being less than about one-tenth as fast as addition of CH_2 for chain growth.

Important are also suppressions of reactions on on-plane-sites

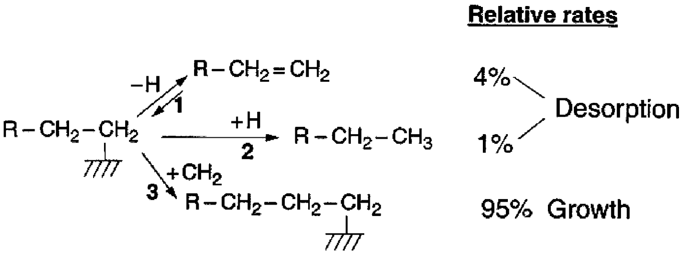

Fig. 2. Alternative FT-alkyl reactions.

(1) Only minor methane formation on on-plane-sites.
(2) Secondary olefin reactions of hydrogenation and double bond shift suppressed but still performing.

4. Spatial constraints

On on-top-sites

(1) Strongly preferred α-attachment of alkyls to the catalyst.
(2) Readsorption of olefins “only” on C-atom one for linear alkyl formation.
(3) Readsorption of “only” olefins (1) from their mixtures with internal olefins.
(4) Suppression of desorption (olefins and paraffins) after the reaction of chain branching.

On on-plane-sites

Preferred (secondary) hydrogenation of α-olefins from their mixture with β-olefins.

5. Concluding remark

It is expected that this brief outline of the concept of Fischer–Tropsch catalysis with its intrinsic features of frustrated reactions and spatial constraints, will certainly be further substantiated through future experimental and theoretical work and it is anticipated that by this chemical approach the nature of working sites in Fischer–Tropsch synthesis will be more clearly understood.

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