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Reflections on the Fischer-Tropsch synthesis: Mechanistic issues from a surface science perspective

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ABSTRACT

The current paper presents a mechanistic view on important steps in the Fischer-Tropsch synthesis on cobalt catalysts, inspired by surface science studies. By revisiting the relation between activity and selectivity that results from the ASF assumption we highlight that knowledge about the number of growing chains as well as their residence time (\sim growth rate) is of crucial importance to sketch a physically realistic scenario for FTS. This motivates further investigations into the microscopic scenario for FTS chain growth on fcc cobalt nanoparticles, by looking into the reaction mechanism in relation to surface structure and by determining the activation energies for key elementary steps. Such studies indicate that the modest activity of Co FTS catalysts might very well be attributable to the difficulty to remove chemisorbed oxygen from the metallic surface, rather than to dissociation of CO, which was found to proceed readily at step edge sites. Chain growth is envisaged to take place on the close-packed surfaces, with chain initiation via $\text{CH} + \text{CH}$ to form acetylene, followed by hydrogenation to form ethylidyne, $\text{C}-\text{CH}_3$, a reaction that is shown to be promoted by co-adsorbed CO. Ethylidyne then couples with CH to form propyne, $\text{HC}-\text{C}-\text{CH}_3$, etc. We propose that a fairly large number of surface sites is involved in the growth of a single chain. In such a "growth ensemble" multiple active step sites produce CH_x monomer species that spill over onto the same close-packed coupling terrace, where one or only a few chains grow at the same time. In such a scenario diffusion of hydrocarbonaceous surface species is an essential step in the overall reaction sequence. We explore which factors need to be taken into account when considering of C_xH_y species under realistic reaction conditions. In addition, we note that the coupling reaction itself, via $\text{CH} + \text{C}-\text{C}_n\text{H}_{2n+1}$, is a source of growing chain mobility.

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1. Introduction

The impressive oeuvre of Professors Mark Dry and Hans Schulz, and the frequent personal contacts with these eminent experts on Fischer-Tropsch synthesis have been a long-time source of inspiration for us. It is an honor to dedicate this paper to both of them [1–4].

Although technologically well-developed, the reaction mechanism of the Fischer-Tropsch synthesis, in which a simple mixture of hydrogen and CO is converted into a diverse mixture of hydrocarbonaceous species, can be ranked among the most complex in the chemical industry, [1]. Empirical studies have provided insights into how catalyst activity and selectivity depend on process param-

eters such as the chemical nature and exact composition of the catalyst material, operating temperature, partial pressures of reactants and products (e.g. water) and the conversion level [3].

On a fundamental level the catalyst has to be active for four distinctly different types of surface reactions: (i) dissociation of H_2 and of the strong CO bond, (ii) removal of surface oxygen as water (or CO_2) (iii) carbon-carbon coupling and (iv) hydrogenation(/dehydrogenation) of C_1H_x and C_yH_z species.

Cobalt and ruthenium most likely perform these functions in the metallic state, where typical catalysts consist of supported nanoparticles. Although the ideal cobalt crystallite size is reported to be around ~ 5 nm [5,6], in practice a metallic crystallite diameter of ~ 10 nm is more representative for supported Co catalysts. For these metallic systems an ongoing topic of debate concerns the geometry of the surface site responsible for the CO bond breaking step, and whether or not the reaction involves CH_xOH_y intermediates. In recent studies regarding the FTS mechanism, density

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functional calculations are typically used to address these questions. The suggestions made based on this approach vary from direct or hydrogen-assisted CO dissociation at step sites with a specific geometry [7], e.g. B5 sites, to hydrogen-assisted CO dissociation on terrace sites [8,9], and CO bond scission after insertion of a CO molecule into the growing chain [9,10].

A second topic of debate is the mechanism of chain growth, where similar questions are debated: which surface structure is optimal for chain growth, and, in close connection to this, what is the chemical nature of the inserting monomer and the coupling intermediate. A number of proposals involving insertion of species such as CH_x ($x=0,1,2$) or CO into growing chains of various types (e.g. alkyls, alkenyls, etc) have been made, where organometallic chemistry has been used for inspiration [11,12]. In the case of iron, the active phase is a carbide, where the lattice carbon atoms in the surface region are likely to be involved in the reaction mechanism [13–17]. Nevertheless, similar mechanistic issues play a role as in the mechanism over metallic FTS catalysts. Experimental approaches using model catalysts, co-feeding studies or transient techniques have been used to obtain insights into mechanistic details of the Fischer-Tropsch chain growth reaction [18–21]. More recently, theoretical calculations using ideal surface structures have been used to study the mechanism on the molecular level [8,22,23]. The experimental counterpart of this, surface science using single crystal surfaces, has rarely been employed for the cobalt system, although there are many opportunities for decisive studies on relevant elementary steps in the mechanism, particularly if such experiments are complemented by state-of-the-art computational studies [24].

The purpose of the present paper is to present a mechanistic view on important reaction steps in the FTS on cobalt, which is largely inspired by surface science experiments from either our own group, or from published literature. When available we make use of data obtained on cobalt surfaces, but as these studies are not very abundant we also make use of findings on nickel and ruthenium single crystal surfaces. The mechanistic picture we sketch is not conclusive, but rests in part on experimental evidence. We hope it may serve as a useful contribution to the discussion and a source of inspiration for future work.

2. FTS activity and selectivity in relation to elementary surface reaction steps

We start our mechanistic discussion with a consideration on the concentration of monomers, growing chains, and residence times of these species. The Anderson-Schulz-Flory distribution describes the FTS product selectivity on the basis of a chain-length independent chain growth probability (α).¹ For a given value of α the value of C_n , the fraction of product molecules with chain length n , can be calculated via [25]:

$$C_n = (1 - \alpha)\alpha^{(n-1)} \quad (1)$$

The average carbon number can then be calculated by multiplying each fraction with its chain length and a summation over all chain lengths:

$$\langle L_n \rangle = \sum_1^\infty n(1 - \alpha)\alpha^{(n-1)} \quad (2)$$

which, for $\alpha < 1$, converges to:

$$\langle L_n \rangle = \frac{1}{1 - \alpha} \quad (3)$$

¹ It should be noted that in reality the product distribution deviates from the ideal ASF distribution. The most notable deviations are a higher than predicted methane selectivity, a lower than predicted C_2 selectivity and slightly (or significantly for Fe catalysts operated in the LT-FT regime) lower alpha for the lighter products [3,25].

Table 1

Relations between the Anderson-Schulz-Flory chain growth probability (α) and selectivity, expressed as number-averaged carbon number ($\langle L_n \rangle$), weight-averaged carbon number ($\langle L_w \rangle$), methane and C_{5+} selectivity, respectively.

α	$\langle L_n \rangle$	$\langle L_w \rangle$	C_{5+} (wt%)	CH_4 selectivity (wt%)
0.5	2	3	19	25
0.75	4	7	63	6.2
0.8	5	9	74	4
0.9	10	19	92	1
0.95	20	39	98	0.25

In applied FTS it is more common to express selectivity on a weight basis. Within the ASF approximation the weight fraction of a product with n carbon atoms, W_n , is defined as:

$$W_n = \frac{n(1 - \alpha)\alpha^{(n-1)}}{\sum_1^\infty n(1 - \alpha)\alpha^{(n-1)}} \quad (4)$$

As the denominator in Eq. (4) is $\langle L_n \rangle$, combining Eqs. (3) and (4) yields:

$$W_n = n(1 - \alpha)^2\alpha^{(n-1)} \quad (5)$$

The weight-averaged carbon number is defined as:

$$\langle L_w \rangle = \sum_1^\infty n^2(1 - \alpha)^2\alpha^{(n-1)} \quad (6)$$

When written out in full, this reduces to:

$$\langle L_w \rangle = 1 + 2\alpha + 2\alpha^2 + 2\alpha^3 + \dots (2\alpha^n) \quad (7)$$

This is variation of the infinite sum $S = \sum_1^\infty x^n$, related via:

$$\langle L_w \rangle = 2S + 1 \quad (7)$$

As $S = \frac{x}{1-x}$ for $x < 1$ the expression then becomes:

$$\langle L_w \rangle = \frac{2\alpha}{1 - \alpha} + \frac{1 - \alpha}{1 - \alpha} = \frac{2\alpha + 1 - \alpha}{1 - \alpha} = \frac{1 + \alpha}{1 - \alpha} \quad (8)$$

Table 1 lists a few examples of the values of $\langle L_n \rangle$ and $\langle L_w \rangle$, as well as the often-used methane and C_{5+} selectivities, for a number of different α values.

We can use the relation between $\langle L_n \rangle$ and α derived in the previous paragraph to establish a link between the surface specific activity (turnover frequency, mole CO converted per mole Co surface atoms) and selectivity at steady state. For example, when $\alpha=0.9$ the average carbon number is 10, i.e. on average 10 monomers are consumed in the time that one product molecule forms and desorbs. More generally speaking, the number-averaged carbon number $\langle L_n \rangle$ can be defined as the ratio of the surface-specific monomer formation rate (r_{CO} , CO molecules converted per mole $\text{Co}_{\text{surf}} \text{ s}^{-1}$) and the surface-specific rate of product formation (mole of product produced per mole $\text{Co}_{\text{surf}} \text{ s}^{-1}$, r_{term}):

$$\langle L_n \rangle = \frac{r_{\text{CO}}}{r_{\text{term}}} \quad (9)$$

This expression can be rewritten in terms of growing chain concentration, θ_{chain} (ML), and the residence time, τ_{chain} (s), of a chain on the surface:

$$r_{\text{term}} = k_{\text{term}}\theta_{\text{chain}} = \frac{\theta_{\text{chain}}}{\tau_{\text{chain}}} \quad (10)$$

Combining Eqs. (3), (9) and (10) yields a mathematical relation between selectivity and surface-specific activity within the ASF approximation [26]:

$$\langle L_n \rangle = \frac{\tau_{\text{chain}}r_{\text{CO}}}{\theta_{\text{chain}}} = \frac{1}{1 - \alpha} \quad (11)$$

This expression shows that, mathematically speaking, a given combination of activity and selectivity can be produced for a variety of values of the chain concentration and the chain residence time as

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