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Metal Particle Size Distributions and Fischer–Tropsch Selectivity. An Extended Schulz–Flory Model

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A new model is presented which accounts for all possible Fischer–Tropsch product distributions. By proper selection of the critical parameters, namely, polymerization growth rate, average particle size of the metal particles which catalyze the reaction, and width of the size distribution, all published Fischer–Tropsch product distributions can be fitted very closely. The method correctly predicts the amount of these carbon numbers which usually deviate strongly from Schulz–Flory kinetics. The model is based on the assumption that a particle size effect exists. On a given size only molecules lower than a given carbon number can be synthesized. On each particle polymerization occurs according to Schulz–Flory kinetics.

INTRODUCTION

The very vivid activity in Fischer–Tropsch (FT) research during the last 5 years has focused mainly on the improvement of catalyst selectivity. It was reasoned that high catalyst selectivity would encourage the synthesis of petrochemical feedstocks from carbon sources other than crude oil (*1*).

With a few exceptions, most of the published hydrocarbon product distributions from a FT synthesis can be fairly accurately described by the Anderson formalism (*2, 3*) or by the so-called Schulz–Flory (SF) polymerization equation (*4*). Madon (*5*) recently showed that mathematically both treatments are identical. Chemically, these schemes represent simple chain growth models in which one-carbon species are added to the end of a growing chain. The schemes assume that growth constants are independent of carbon number. The Anderson growth scheme (*2*) also predicts isomer distributions for a given carbon number by introducing a second constant. More recently a 3-constant scheme was advanced in order to be able to predict the distribution of ethyl isomers next to methyl-substituted carbon chains (*3*).

If the SF equation is fitted to FT products of a wide carbon number range, it is striking that marked deviations always exist in the C_2–C_4 carbon number range. Therefore, pure empirical modifications of the SF equation have been proposed to account for this (*6*). These modifications allow for secondary cracking of products, branching selectivity, and reincorporation of short olefins by chain initiation and propagation. If the hydrocarbon synthesis gives a narrower carbon number distribution, the SF law agrees better in the C_3–C_4 product range (*7, 8*), but C_2 always deviates.

In recent literature, however, selective formation of FT products is reported for Ru, Co, and Fe, either supported on alumina or zeolites (*5, 9–12*). In these cases chain growth is dependent on chain length and the product spectrum can no longer be fitted to a SF equation. In the case of two-component catalysts (*13*) the improved selectivity is entirely due to secondary acid-catalyzed reactions of primary FT products on a shape-selective zeolite. On the large pore zeolites, secondary cracking reactions and diffusion effects could be ruled out completely (*9, 10*) and qualitatively a cor-

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relation was established between the size distribution of the catalyst metal particles and the carbon number distribution of the FT products. Moreover, it was claimed that FT synthesis of hydrocarbons can be used as a gentle method to obtain information on the size distribution of alloys (*14*). The only prerequisite is that the catalyst and the reaction conditions allow that high growth rates of the polymerizing entities can be reached (*14*).

All this clearly shows that neither the SF model nor the Anderson growth scheme can be of general use to describe sufficiently FT selectivity. Therefore, there is need for a new model which can account both for the SF-type product distributions and for the hydrocarbons obtained on the more selective catalysts. Such a model is advanced here and was constructed using the basic assumption that a particle size effect rules FT selectivity. The model is compatible with all published FT product distributions.

EXTENDED SF MODEL

Physical Basis for the Model

The following concepts are at the basis of this new model:

i. Any metal particle of a given size or any ensemble of metal surface atoms (as in alloys) imposes a strict maximum upon the chain length of the hydrocarbons which can be formed on it. This assumption is based upon experimental evidence (*9, 10*). Indeed, Ru metal particles encaged in zeolite Y crystals of 1.5 and 3–4 nm were found to terminate the hydrocarbon chain length at carbon numbers 5 and 11–12, respectively.

The implications of this assumption on a mechanistic basis are rather severe. Any mechanism which proposes a one-by-one insertion of C_1 species in a metal–alkyl chain has to be ruled out. Any proposed mechanism which assumes a flatly adsorbed alkyl chain or an end-to-end attachment of alkyl and/or oxygenated species (*15, 16*) agrees with this assumption.

ii. The reaction mechanism can be formally described by a polymerization scheme in which the number of polymerization steps is governed by the first assumption. This implies that SF kinetics are obeyed on any metal particle. The maximum chain length of the hydrocarbon formed on each particle is determined by its size or by the number and arrangement of surface atoms. This maximum chain length is reached only for the highest chain growth probabilities which can be obtained experimentally. At low degrees of polymerization, it is expected that this maximum chain length cannot be formed.

iii. The molar amount of hydrocarbons formed on any particle remains constant and at any moment only one chain is growing on each metal particle. As a result of this it is understood why the turnover number for CO disappearance (number of CO molecules reacting per second and per surface metal atom) increases with metal particle size, as is observed experimentally (*18*).

iv. A linear relationship exists between particle size and the maximum hydrocarbon chain length which can be formed on it. Since linear 1-olefins are generally accepted to be primary products in a FT synthesis (*7*), it is likely that the longest linear distance on a catalytic site relates to the maximum hydrocarbon chain length rather than to its surface. The proportionality factor between both properties is again unknown but is not important for calculations on a relative basis.

Mathematical Formulation

The weight fraction (W_n) of carbon number n in terms of Schulz–Flory kinetics is related to the probability of chain growth α as follows:

$$W_n = n(1 - \alpha)^2\alpha^{n-1}. \tag{1}$$

The α factor is by definition related to the average degree of polymerization (Q) and to the rate of propagation (r_p) and termination (r_t) of the chain process as follows:

$$Q \equiv (r_p + r_t)/r_t = 1/(1 - \alpha). \qquad (2)$$

The value of Q is determined on one hand by the catalyst (metal) characteristics and on the other hand by the experimental conditions such as reaction temperature, CO/H_2 ratio in the feed, and absolute reaction pressure.

If on a metal particle of a given size FT products of maximum size N can be formed, Concepts (i) and (ii) above are mathematically translated as follows:

$$W_n/n \quad \alpha^{n-1}(1 - \alpha)^2 \qquad \text{for } n < N. \qquad (3)$$

The hydrocarbon mole fraction with carbon atom N then equals:

$$W_N/N = 1 - \sum_{1}^{N-1} \alpha^{n-1}(1 - \alpha)^2. \qquad (4)$$

In this way the FT hydrocarbon distribution can be calculated for a metal particle of a given size.

For the particle size distribution (P_d) a skewed Gaussian type curve is given in the literature (*17*):

$$P_d = \frac{2}{(2\pi)^{1/2} d \ln \sigma} \exp\left[-\frac{1}{2}\left(\frac{\ln d/2 - \ln \bar{d}/2}{\ln \sigma}\right)^2\right]. \qquad (5)$$

In this equation d is the particle diameter, $\bar{d}$ the geometric mean of the distribution, and σ the square root of the variance of the distribution. The abundance of particles with diameter d can be calculated provided the mean particle size and the variance are known. This equation is used for all values of d to fit FT product distributions from metals on nonzeolitic supports. For zeolites, it is thought that particles are encaged in the pores and a maximum value is imposed by the framework upon the metal particle size. Experimental evidence is present for this (*14*, *19*). Mathematically this results in the following restriction on the d values which have to be used in Eq. (5):

$$0 < d \leq \bar{d}. \qquad (6)$$

Concept (iv) can be quantified as follows:

$$d = AD_N \qquad (7)$$

where D_N is the diameter of the particle which in terms of carbon numbers is able to produce hydrocarbons of maximum size N, and A is a proportionality factor.

Using Eqs. (3) and (4) the product distribution in terms of carbon numbers on a single metal particle can be calculated. This can be done for the whole distribution of particles determined by Eqs. (5) and (7) or (5), (6), and (7) by simple summation of the W_n/n values. The problem was solved numerically. The three parameters, α, σ, and $\bar{d}$, were optimized either manually by a trial and error procedure using physically acceptable values or by a least squares method.

In all cases there was good agreement between the parameters obtained in both ways.

RESULTS

Prediction of FT Distributions Which Deviate from Formal SF Kinetics

The extended Schulz–Flory (ESF) method has been used to fit an experimental FT product distribution published by Madon (*5*) for Ru on alumina. The results are shown in Fig. 1. The plot shows that the deviation from classical SF kinetics is important and in no way can serve as an accurate description of the observed phenomena. Using the aforementioned equations a satisfactory prediction of the experimental data can be obtained. Therefore a skewed Gaussian distribution was used with an average particle size corresponding to $\overline{D_N} = 10$, a rather narrow variance of 1.56 and a growth probability of 0.95. This high growth probability is very reasonable for Ru at the high pressure of 3.11 MN m^{-2} used in this experiment.

Figure 2 shows the non-SF distribution of FT products for Co on alumina with two different pore sizes (*11*) together with the best fit of the product distribution using the

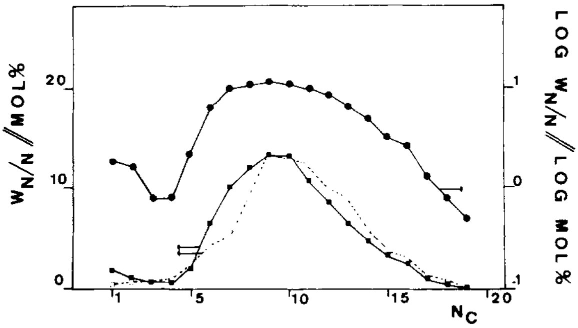

FIG. 1. FT hydrocarbon distribution (W_N/N) against carbon number (N_c) for 1% Ru on alumina. Full lines represent the experimental data from Ref. (5); the dotted lines represent the product distribution according to the ESF method.

ESF method. Also shown are the particle size distributions in relative units used to fit these data. The agreement is rather close. Both catalysts are identical except for the average pore size of the support. It is very satisfactory that both distributions can be fitted using the same growth probability (α = 0.89) but different values for σ of 1.44 and 2.10 and for $\overline{D_N}$ of 4 and 17 are obtained, respectively. These distributions do not seem to be unreasonable but unfortunately no direct measurements of the particle sizes are available. The pore size distribution is important insofar that it may impose a maximum size on the metal particles which are formed in it.

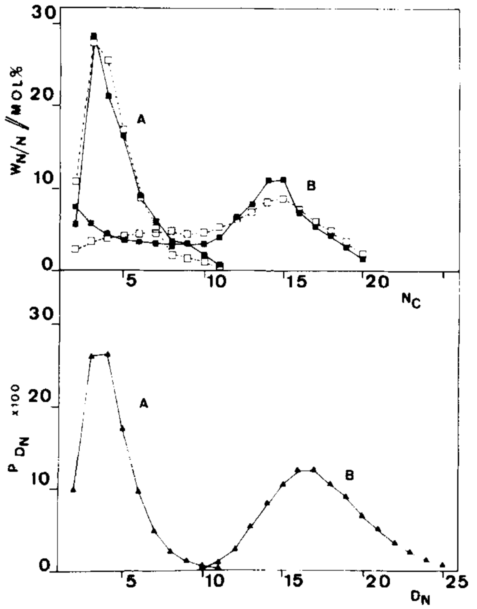

FIG. 2. Upper part: FT product distribution against carbon number for Co on alumina (Ref. (11)) (closed symbols) and predicted by ESF (open symbols). Lower part: Particle size distribution (P_{D_N}) among relative diameter of particles (D_N) used to fit the FT results. (A) For 2% Co on alumina with mean pore radius of 6.5 nm; (B) for 2% Co on alumina with average pore radius of 30 nm.

Product distributions which also strongly deviate from classical SF kinetics are shown in Fig. 3 for RuLaY and RuNaY zeolites (9, 10). A satisfactory fit is obtained in both cases if a growth probability of 0.85 and 0.77 is used, respectively. For

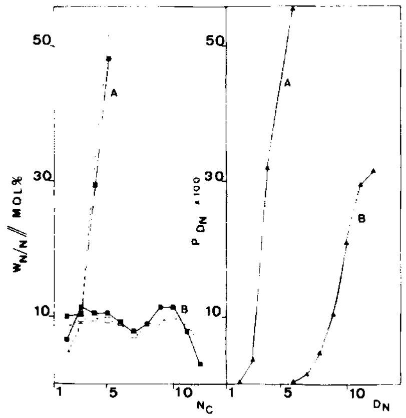

FIG. 3. Left part: FT product distribution against carbon number for RuLaY (A) and RuNaY (B) zeolites (Ref. (10)) and predicted by ESF. Right part: Particle size distributions used to fit the respective product distributions.

σ, values of 0.75 and 1.8 are used and for $\overline{D_N}$ values of 5 and 12, respectively. A near-monodispersion of Ru particles can be used to fit the observed products. This is in agreement with the results from chemical and physicochemical measurements from which it was deduced that Ru was encaged in the supercages (1.5 nm) of LaY zeolite and in holes of the structure in the case of NaY (3–4 nm)(*19*).

Prediction of FT Products Which Formally Follow SF Kinetics

In Fig. 4 two hypothetical particle size distributions are used to predict FT product distributions using the ESF method. A narrow particle size distribution with large mean particle size and low growth probability (α = 0.70; σ = 1.1; $\overline{D_N}$ = 40) is compared with a second broader distribution of sizes but with high growth probability (α = 0.85; σ = 4; $\overline{D_N}$ = 35). This situation is often encountered for heavily loaded classical supports. The growth probabilites are typical for ruthenium and iron, respectively.

The synthesized product spectra fit very well to a SF kinetic scheme (Fig. 4, upper part), at least for carbon numbers higher than 4. The deviation at lower carbon numbers is typical and has been observed for numerous real catalysts (*7*, *8*).

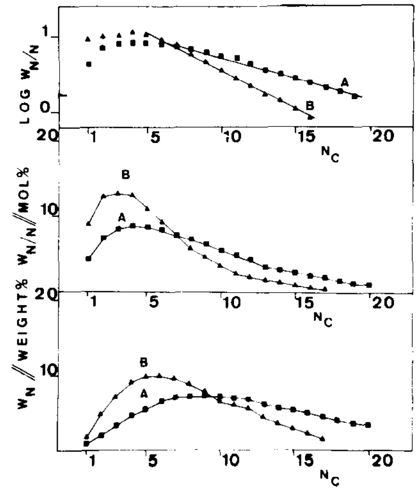

FIG. 4. Product distributions on two hypothetical catalysts using ESF: (A) low growth probability and narrow particle size distribution with large mean particle size (α = 0.7; σ = 1.1; $\overline{D_N}$ = 40); (B) high growth probability for a broad particle size distribution with large mean particle size (α = 0.85; σ = 4; $\overline{D_N}$ = 35).

In Fig. 5, three product distributions taken from the literature are shown. They are generally considered to obey SF kinetics. The deviations at lower carbon numbers are striking in cases A and C. The same product distributions can be generated using the ESF model. Even the deviations at low carbon numbers can be fitted perfectly. The values taken for the particle size distribution and the growth rate are collected in Table 1. For both Co catalysts the same particle size distribution is used. Only the growth factor has to be increased when lower H_2/CO ratios in the feed are

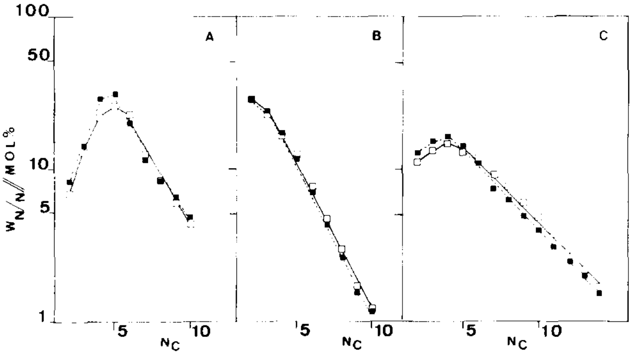

FIG. 5. Fit of experimental product distributions using the ESF method (closed symbols: calculated values; open symbols: measured values). (A) Fe catalyst (Refs. (*7*, *8*)); (B) Co catalyst, H_2/CO = 4 at atmospheric pressure (Ref. (*6*)); (C) same catalyst, H_2/CO = 2 (Ref. (*6*)).

TABLE 1

Characteristics of Metal Particles of FT Catalysts and Reaction Conditions[a] Used to Fit Experimental FT Product Distributions by ESF

Catalyst	Reference	H_2/CO	$\overline{D_N}$	σ	α
Iron	*7, 8*		10	1.8	0.79
Cobalt	*6*	4	15	2.0	0.55
Cobalt	*6*	2	15	2.0	0.70

[a] Data used to fit the product distributions of Figs. 5A, B, and C, respectively.

used. It is perfectly logical that higher CO pressures result in higher growth rates. The product distribution on the iron catalyst can be fitted with a size distribution of average width and a perfectly normal growth factor for iron.

DISCUSSION

Reliability of the ESF Model

It is shown in the figures that the ESF model is of general applicability to fit product distributions from a Fischer–Tropsch synthesis. Very tight fits can be obtained for a wide variety of catalysts and reaction conditions. In this way, the assumptions made to construct the model although being straightforward seem to be verified a posteriori. The method is based on the following main assumptions:

(1) A particle size effect exists in FT synthesis and the geometry of the site determines the maximum chain length of the synthesized products. Experimental evidence exists to support this statement.

(2) On every single particle, the size of the FT products can be described by formal Schulz–Flory kinetics. Numerical values for three parameters are needed to fit experimental product distributions. In any case, the values used for the average metal particle size distribution, width of the distribution, and growth rate of the polymerization process are perfectly normal.

It should be noted that even the ESF model is unable to predict precisely the amount of methane formed. Deviations from any polymerization scheme are to be expected. Indeed, substantial evidence now exists that two different intermediates can lead to methane formation, one of which cannot participate in the polymerization process (*20, 21*). This explains why even with the ESF model too low methane concentrations are predicted.

Requirements for Selective Fischer–Tropsch Catalysts

From the results presented it can be derived that to obtain product distributions which substantially deviate from SF kinetics and which tend to be more selective, two conditions must necessarily be fulfilled:

(1) A very narrow metal particle size distribution is needed. Broad particle size distributions tend to produce FT products with a very wide carbon number distribution and a not too well pronounced maximum. At higher growth probabilities the plots of P_{D_N} against D_N and W_N/N against N_C almost coincide. A homogeneous distribution of nearly identical surface ensembles can be obtained by chemical means such as alloying and surface dilution (*14*).

(2) Only when high growth probabilities of the growing chain can be realized ($\alpha > 0.8$) can deviations from SF kinetics be observed. This can partly be done by the right choice of the reaction parameters. The present work shows that this can be obtained on ruthenium and cobalt-based catalysts irrespective of the support (*9–11*). This criterion reflects the effects of chemical parameters such as the presence of promoters and the nature of the FT active element.

The improved selectivities which have been collected from the literature in the present paper are due to primary effects at the level of the active site. Secondary effects such as diffusion, secondary cracking, and hydrogenolysis reactions can definitely be excluded. The results on the two zeolite-based catalysts rule out diffusional effects as determining selectivity. In the structure of zeolite Y, the same product distribution should be expected irrespective of the size of the metal particles. Secondary cracking and hydrogenolysis of long-chain 1-olefins under reaction conditions have been ruled out experimentally (*10*).

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