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# A new product distribution formulation for Fischer–Tropsch synthesis. Effect of metal crystallite size distribution

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A new product distribution formulation is presented for Fischer–Tropsch synthesis (FTS). This formulation, which contains the effect of the metal crystallite size on the product selectivity, can explain all possible Fischer–Tropsch product distributions. The Anderson–Shulz–Flory distribution formulation can be regarded as its approximation in special cases.

**Keywords:** Fischer–Tropsch synthesis; product distribution; effect of crystallite size; chain growth; mechanism

## 1. Introduction

In the past 50 years, a lot of work has been done on the mechanism of the growth of the carbon chain in Fischer–Tropsch synthesis. The history of the development of this mechanism can be divided into two stages [1]:

(1) Chain growth through lateral reaction between building blocks populating the catalyst surface.

(2) Chain growth through stepwise insertion of one building block per step.

The first model was proposed in 1939 by Craxford and Rideal [2]. This mechanism failed to explain the fact that there were only a relatively small fraction of branched chain hydrocarbons in FTS products [3].

The concept of stepwise insertion was introduced in 1946 by Herington [4]. He was the first to quantify the molar distribution of a synthesis reaction. The same formulation was independently presented by Anderson et al. in 1951 [5], and recognized by the Olives in 1976 [6], who ascribed to it the name Anderson–Shulz–Flory (ASF). This model yields a linear plot of the logarithm of weight of product versus carbon number.

As these ideas developed, a number of mechanistic proposals were made regarding the nature and behavior of surface species in reaction [7–13]. Except for a couple of formulations which extend this approach to branched chains and to short-chain alcohols [14–16], little progress has been made beyond this stage.

The ASF distribution formulation accords with most experimental results. Only the product with very short chains may deviate from the linear plot. However, in recent years, a number of papers suggest that the FTS products on ultrafine particle catalysts do not obey the ASF distribution. It has been found that the carbon-number distribution is related to the size of the metal crystallite, particularly, that the length of the growing chain is limited by the dimension of the metal crystallite [17–23].

All this clearly shows that there is need for a new model which can account for both the ASF-type distribution and the hydrocarbons obtained on more selective catalysts. Such a model is proposed here, in which a quantitive correlation is established between the size distribution of the catalyst metal crystallites and the carbon number distribution of the products. The new product distribution formulation predicts satisfactorily the FTS product distribution on small crystallite metal catalysts, and the ASF formulation is its approximation on large crystallite catalysts.

## 2. Theory and mathematical formulation

The new model is based on the following two assumptions:

(1) On any metal crystallite surface of a given size only molecules lower than a given carbon number can be synthesized.

(2) Though, on the whole, the FTS products on small crystallite catalysts do not obey the ASF distribution, the products on each surface of the metal crystallite do.

In ASF theory, the chain propagation is represented by

$$\Phi_n = \Phi_1 \alpha^{n-1}, \tag{1}$$

where $\Phi_n$ is the mole fraction of the product containing $n$ carbons and $\alpha$ is the probability of chain growth. This formula is only suitable for the FTS products on large crystallite metal catalysts. In order to take the effect of the size of metal crystallite on the carbon chain length into consideration, a size distribution function $q(A_n)$ is imposed on the ASF formula,

$$\Phi_n = \Phi_1 \alpha^{n-1} q(A_n), \tag{2}$$

$$\log \Phi_n = \log \Phi_1 + (n-1) \log \alpha + \log q(A_n), \tag{3}$$

where $A_n$ is an area of a given size, and on any metal crystallite surface of this size only molecules with $n$ or lower than $n$ carbons can be formed. $q(A_n)$ is the

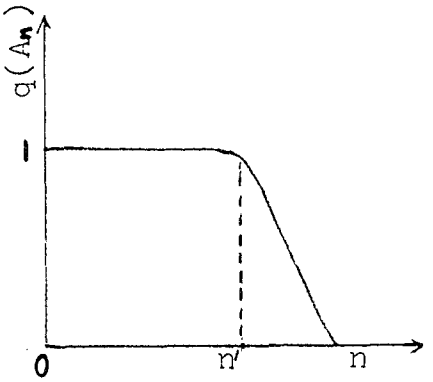

Fig. 1. Distribution shape of $q(A_n)$.

fraction of these metal crystallite surfaces which are equal to or larger than $A_n$. In other words $q(A_n)$ is the fraction of those metal crystallite surfaces on which molecules with $n$ carbons are synthesized.

## 3. Discussion

In the above formulation, the last term $\log q(A_n)$ is a revision to the ASF distribution. It represents the effect on the selectivity of products caused by the size distribution of the catalyst metal crystallite surfaces.

The changeable range of $q(A_n)$ is $0 < q(A_n) \leqslant 1$. $q(A_n)$ decreases with increasing carbon number $n$ as shown in fig. 1. As for the lighter molecules ($n < n'$), they are synthesized on almost all catalyst metal crystallite surfaces. In this case, $q(A_n) = 1$, $\log q(A_n) = 0$, the products obey the ASF distribution, which yields a linear plot of the logarithm of yield of product versus carbon number. As for larger molecules ($n > n'$), they are only synthesized on some larger metal crystallite surfaces. Under this condition, $q(A_n) < 1$, $\log q(A_n) < 0$, the products deviate from the ASF distribution. In conclusion, for the FTS on small metal crystallite catalysts, this mathematical treatment describes a situation of product distribution that is represented in fig. 2. It should be observed that $\log \Phi_n$ begins to fall below the ASF straight line around a specific carbon number $n'$ and because of $q(A_n)$ being a decreasing function of carbon number $n$, the deviation will increase with $n$. The precise product distribution curve after $n'$ is related to the functional type of $q(A_n)$. In fig. 2, the dotted line is the extension of the ASF distribution straight line (for $n < n'$). In the absence of the effect of the size of the metal crystallite, the products after $n'$ should be on the extended line.

Compared with some experimental results of FTS on small crystallite metal catalysts [21–23], there is a good agreement between the experimental results

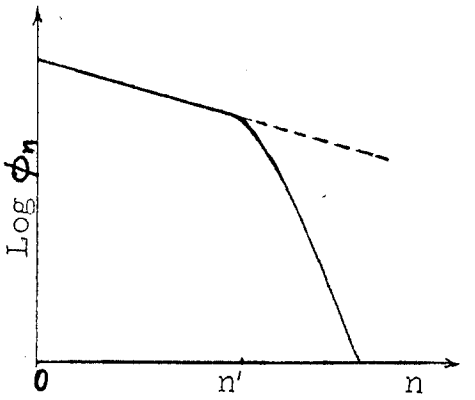


Fig. 2. FT product distribution predicted by formula (3) for small crystallite metal catalysts.

and our theoretical prediction, showing a negative deviation from the ASF distribution after a specific carbon number and that the deviation increases with the carbon number $n$ (see figs. 3–6).

For the Fischer–Tropsch synthesis on large particle catalysts, the metal crystallite surfaces are large enough for the growth of the carbon chain and there is no limitation to the maximum length of the carbon chain caused by the size of the metal crystallites. Under this condition, $q(A_n) = 1$ for all the synthesized products and our distribution formula (3) reduces to the Anderson–Shulz–Flory distribution formula. Therefore, the ASF distribution formula is a special case of our distribution formula (3).

From the definition of $q(A_n)$, there is a direct relation between the function $q(A_n)$ and the size distribution of the catalyst metal crystallites. Combining with

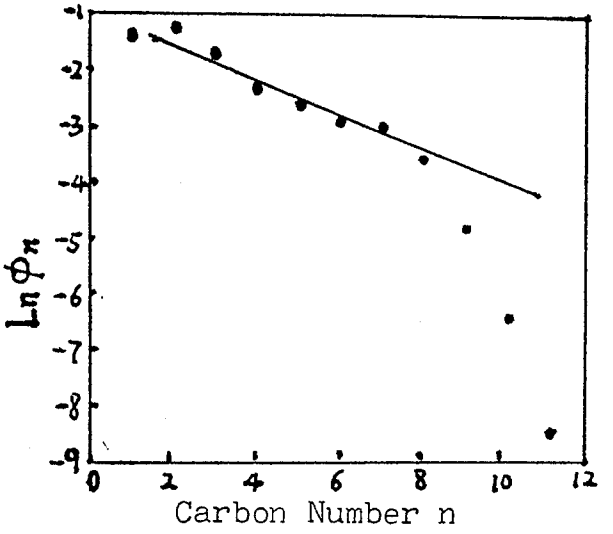


Fig. 3. FT product distribution on 3% Fe/C (ref. [22]).

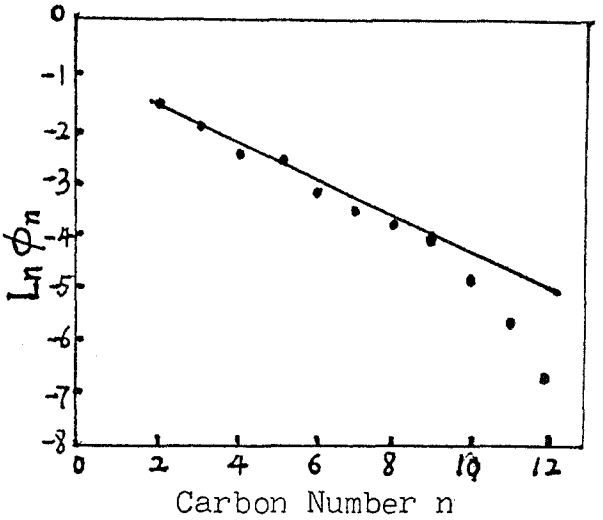


Fig. 4. FT product distribution on 10% Fe/C (ref. [22]).

the discussion above we arrive at the following conclusions: According to formula (3), with a known distribution function of the size of the catalyst metal crystallites, we can quantitively predict the product distribution on them. Conversely, from the log $q(A_n)$ obtained in experiments, the size distribution of the catalyst metal crystallites could be estimated.

When the new distribution formula (3) is used to fit the experimental results on Fe/C by Jones et al. [22], good agreement is achieved. In their work, a series of FTS were done for the Fe/C catalysts with different size distributions of the metal crystallites. First, from the product distribution on Fe/C (10%), a relation

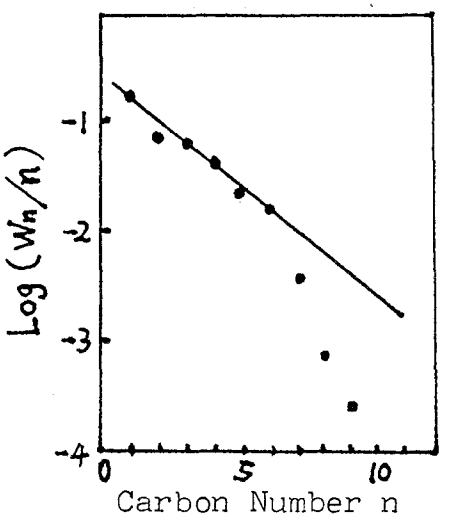


Fig. 5. FT product distribution on Fe–Cs/ZSM-5 (ref. [21]).

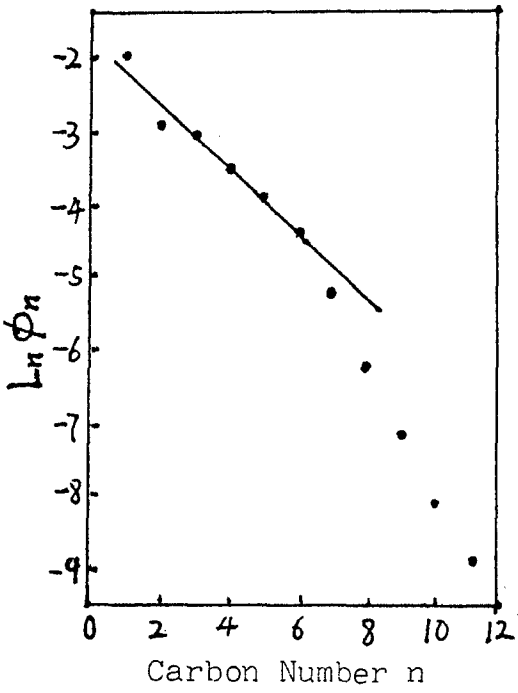


Fig. 6. FT product distribution on Fe/Ca (ref. [23]).

is established between the size of the metal crystallite and the maximum carbon number of hydrocarbons synthesized on it. The results are listed in table 1. For example, hydrocarbons with 10 carbons can only be synthesized on metal crystallites which have a size of diameter of more than 4.1 nm. And then, we use the relation above to correlate another experiment on Fe/C (3%) and to predict the size distribution of the metal crystallites. From the calculated results (listed in table 2), we see that for the Fe/C (3%) about 32% of the metal crystallites have the size of more than 1.5 nm in diameter and only 9% have the size of more than 4.1 nm. From this we estimate that the average size in diameter is about 1 nm. The result measured with TEM is less than 1.1 nm [22]. Considering

Table 1
Correlation of the results of metal crystallites distribution and FTS product distribution on Fe/C (10%) with formula (3)

| | Carbon number | | | |
|---|---|---|---|---|
| | 9 | 10 | 11 | 12 |
| ln $q(A_n)$ | −0.05 | −0.43 | −0.86 | −1.57 |
| $q(A_n)$ | 0.95 | 0.65 | 0.42 | 0.21 |
| metal crystallite diameter (nm) | 1.5 | 4.1 | 6.3 | 10 |

Table 2
Correlation of the results of metal crystallites distribution and FTS product distribution on Fe/C (3%) with formula (3)

| | Carbon number | | |
|---|---|---|---|
| | 9 | 10 | 11 |
| $\ln q(A_n)$ | −1.14 | −2.43 | −4.29 |
| $q(A_n)$ | 0.32 | 0.09 | 0.01 |
| metal crystallite diameter (nm) | 1.5 | 4.1 | 6.3 |

the statistical nature of particle size in the experiment and the rather simplified postulate of chain growth mechanism in the model, the result is satisfactory.

## References

[1] P. Biloen and W.M.H. Sachtler, Adv. Catal. 30 (1981) 165.
[2] S.R. Craxford and E.K. Rideal, J. Chem. Soc. (1939) 1604.
[3] H.H. Storch, Adv. Catal. 1 (1948) 115.
[4] E.F.G. Herington, Chem. Ind. 65 (1946) 246.
[5] R.B. Anderson, R.A. Friedel and H.H. Storch, J. Chem. Phys. 19 (1951) 313.
[6] G. Henrici-Olive and S. Olive, Angew. Chem. Int. Ed. 15 (1976) 136.
[7] A.O.I. Rautaruoma and H.S. van der Baan, Appl. Catal. 1 (1981) 247.
[8] A.T. Bell, Catal. Rev. Sci. Eng. 23 (1981) 203.
[9] V. Ponec, Catal. Rev. Sci. Eng. 18 (1978) 151.
[10] E.L. Mueterties and J. Stein, Chem. Rev. 6 (1979) 479.
[11] C.K. Rofer-Depoorter, Chem. Rev. 81 (1981) 447.
[12] H. Pichler and H. Schulz, Chem. Ing. Tech. 42 (1970) 1162.
[13] V. Ponec and W.A. Barneveld, Ind. Eng. Chem. (RD) 18 (1979) 268.
[14] R.B. Anderson and Y.C. Chan, Adv. Chem. 178 (1979) 113.
[15] R.A. Friedel and R.A. Anderson, J. Phys. Chem. 72 (1950) 1212, 2307.
[16] P. Taylor and B.W. Wojciechowski, Fuel Proc. Technol. 8 (1984) 135.
[17] D. Vanhove, P. Makambo and M. Blanchard, J. Chem. Soc. Chem. Commun. (1979) 605.
[18] H.H. Nijs and P.A. Jacobs, J. Catal. 65 (1980) 328.
[19] M.A. McDonald, D.A. Storm and M. Boudart, J. Catal. 102 (1986) 386.
[20] R.L. Espinoza and R. Snel, J. Chem. Soc. Chem. Commun. (1986) 1796.
[21] T. Mitsudo, H. Boku, S. Murachi, A. Ishihara and Y. Watanabe, Chem. Lett. (1985) 1463.
[22] V.K. Jones, L.R. Neubauer and C.H. Bartholomew, J. Phys. Chem. 90 (1986) 4832.
[23] R. Snel, Catal. Lett. 1 (1988) 327.