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Equations for the Molecular Mass Distribution of Hydrocarbons Formed in CO Hydrogenation on a Cobalt–Zirconium Catalyst

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Abstract—A mathematical model for Fischer–Tropsch synthesis is proposed. The model takes into account the most common deviations from classical Anderson–Schulz–Flory distribution and adequately describes the experimental molecular mass distributions of hydrocarbons formed in carbon monoxide hydrogenation on a cobalt catalyst supported on the zirconium form of silica gel.

The variety of products formed in Fischer–Tropsch synthesis under real conditions prevents one from carrying out standard kinetic and mechanistic studies. However, in many cases, an alternative approach can be used, namely, the development of mechanistic and mathematical models based on the analysis of the molecular mass distribution (MMD) of synthesis products [1]. The approach is based on the Herington postulate [2] on the growth of a C–C bond chain due to the addition of a monocarbon unit to surface intermediates until chain termination occurs. This can be represented as the following scheme:

$$\mathrm{CO + H_2} \longrightarrow \overset{\uparrow \mathrm{C_1}}{ZA_1} \longrightarrow \overset{\uparrow \mathrm{C_2}}{ZA_2} \longrightarrow \ldots \longrightarrow \overset{\uparrow \mathrm{C}_n}{\mathrm{ZA}_n} \longrightarrow \ldots, \qquad \text{(I)}$$

where C_n are the final products containing n carbon atoms, A_n are the surface intermediates, and Z are the active sites of the catalyst surface. The postulate was experimentally confirmed in [3, 4].

When the ratio (β) of the probability of chain termination to that of chain growth is independent of n according to scheme (I), the following relation is valid [2, 5]:

$$\beta = \frac{\phi_n}{\sum_{n+1}^{\infty} \phi_i} = \frac{1-\alpha}{\alpha}, \qquad (1)$$

where ϕ_n and ϕ_i are the numbers of moles of products with a number of carbon atoms equal to n and higher than n, respectively; and α is the probability of C–C bond chain propagation. The Anderson–Schulz–Flory (ASF) equation can be obtained from Eq. (1) [6]:

$$m_n = (1-\alpha)\alpha^{n-1}, \qquad (2)$$

where m_n is the mole fraction of the product containing n carbon atoms.

The reason for which Eq. (1) is fulfilled and the MMD is described by the ASF equation can easily be understood from the following analysis.

It follows from scheme (I) that the following expression can be written for two arbitrarily chosen intermediates A_m and A_n:

$$\frac{\frac{dC_m}{dt}}{\sum_{i=m+1}^{\infty} \frac{dC_i}{dt}} : \frac{\frac{dC_n}{dt}}{\sum_{i=n+1}^{\infty} \frac{dC_i}{dt}} = \left(\frac{k_{\mathrm{term}}^{(m)} \theta_m \Pi\theta_{\mathrm{term}}}{k_{\mathrm{pr}}^{(m)} \theta_m \theta_{\mathrm{A}}}\right) : \left(\frac{k_{\mathrm{term}}^{(n)} \theta_n \Pi\theta_{\mathrm{term}}}{k_{\mathrm{pr}}^{(n)} \theta_n \theta_{\mathrm{A}}}\right) = \frac{k_{\mathrm{term}}^{(m)}}{k_{\mathrm{pr}}^{(m)}} : \frac{k_{\mathrm{term}}^{(n)}}{k_{\mathrm{pr}}^{(n)}}, \qquad (3)$$

where C_m, C_n, and C_i are the molar concentrations of hydrocarbons with a number of carbon atoms equal to m, n, and i, respectively; $k_{\mathrm{term}}^{(m)}$ and $k_{\mathrm{term}}^{(n)}$ are the constants for the rate of their corresponding termination stages, while $k_{\mathrm{pr}}^{(m)}$ and $k_{\mathrm{pr}}^{(n)}$ are the constants for the rate of chain propagation; θ_m and θ_n are the surfaces covered by the intermediates A_m and A_n, respectively; θ_{A} is the surface covered by monocarbon units participating in the chain propagation steps; and $\Pi\theta_{\mathrm{term}}$ is the product of the surfaces covered by compounds (other than the intermediates A_m and A_n) participating in the chain termination steps.

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After transformations, separation of variables, and integration, we have

$$\int_0^{C_m} dC_m \sum_{n+1}^{\infty} \int_0^{C_i} dC_i = \left(\frac{k_{term}^{(m)}}{k_{pr}^{(m)}} : \frac{k_{term}^{(n)}}{k_{pr}^{(n)}} \right) \int_0^{C_n} dC_n \sum_{m+1}^{\infty} \int_0^{C_i} dC_i. \quad (4)$$

Taking into account Eq. (1), we obtain

$$\frac{C_m}{\sum_{m+1}^{\infty} C_i} : \frac{C_n}{\sum_{n+1}^{\infty} C_i} = \frac{k_{term}^{(m)}}{k_{pr}^{(m)}} : \frac{k_{term}^{(n)}}{k_{pr}^{(n)}} = 1 \quad (5)$$

and

$$\frac{k_{term}^{(m)}}{k_{pr}^{(m)}} = \frac{k_{term}^{(n)}}{k_{pr}^{(n)}}. \quad (6)$$

Thus, Eq. (1) is fulfilled at all n, and Eq. (2) is valid because the ratio between the constant for the rate of chain termination and propagation is independent of the chain length and, as a consequence, the kinetic equations describing the ratio between the rates of these steps are identical for all intermediates in scheme (I).[1] Therefore, we can use Eq. (1) to find relationships between the amounts of various products formed in Fischer–Tropsch synthesis or their proportional values. Apparent rates of particular steps of Fischer–Tropsch synthesis can conveniently be used for the development of mathematical models for the synthesis. Mathematical correlations obtained using these values are usually simpler than similar relationships derived from the number of moles of the products formed or their molar concentrations. After Eq. (1) was divided into the time during which the products were formed and into a quantity that characterizes the reaction space (the catalyst surface, weight, etc.), this equation can be presented in the form

$$\frac{1-\alpha}{\alpha} = \frac{w_{term,\,n}}{w_{pr,\,n}},$$

where $w_{term,\,n}$ and $w_{pr,\,n}$ are the apparent rates (henceforth, for brevity, rates) of chain termination and propagation, respectively. From this, taking into account the material balance equations

$$w_{pr,\,n} = w_{pr,\,n+1} + w_{term,\,n+1},$$

we have the relations

$$w_{pr,\,n+1} = w_{pr,\,n}\alpha, \quad (7a)$$

$$w_{term,\,n+1} = w_{pr,\,n}(1-\alpha). \quad (7b)$$

Thus, if the MMD of hydrocarbons obeys the ASF equation, the mechanism can be developed from the results of one experiment, and the rates of all steps in this mechanism can be determined from the overall rate of hydrocarbon formation (w_0) using Eqs. (7a) and (7b).

However, the MMD of hydrocarbons is not always described by the ASF equation. This fact gave rise to several works [1] considering the MMD resulting from various complications of the scheme (I). Unfortunately, these models were not adequately confirmed experimentally because the complications were based on hypothetical reactions. Nevertheless, works of this kind showed that it is, in principle, possible to study the mechanism of the Fischer–Tropsch synthesis based on more complicated distributions than the Anderson–Schulz–Flory MMD.

The experimental distributions were studied in parallel [1]. In these cases, the number of developed mechanisms and mathematical models describing the MMD of hydrocarbons is much lower. However, these works made it possible to reveal the most frequent deviations from the ASF MMD. These are, first and foremost, an overestimated (sometimes underestimated [7]) concentration of C_1 hydrocarbons, an underestimated concentration of C_2 hydrocarbons, and a nonlinear distribution. Situations where one, or simultaneously two, of such deviations occur are so abundant that there is no doubt that they are not random and, hence, should be taken into account in the mechanism of Fischer–Tropsch synthesis and in MMD equations.

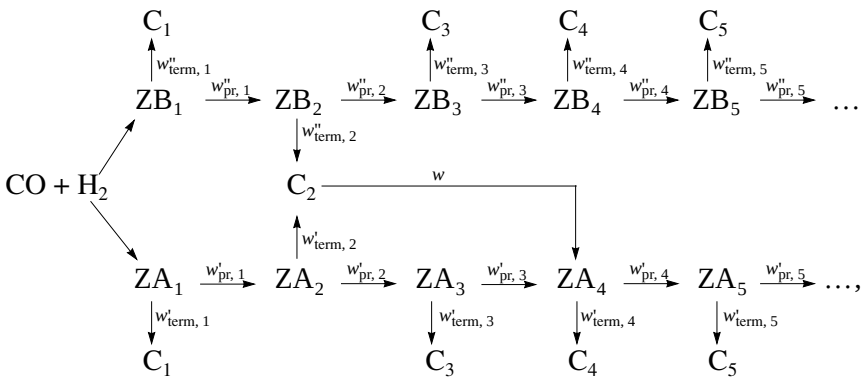
It was found previously [8] that the MMD of C_{4+} hydrocarbons formed during CO hydrogenation on the $Co/SiO_2 \cdot Zr(IV)$ catalyst (a cobalt catalyst supported on the zirconium form of silica gel) is nonlinear and satisfies the model of chain growth via two parallel routes with different α values ($\alpha_1 < \alpha_2$). The difference in the probabilities of C–C bond chain propagation can be attributed to the following two reasons: (1) chain growth occurs at two different catalyst sites [9] and (2) chain growth occurs via different mechanisms through two types of intermediates [10, 11]. The MMDs of hydrocarbons are identical in both cases [11].

Despite the fact that C–C bond chain growth via two parallel routes was initially explained by the presence of two types of active sites on the catalyst surface [9], convincing arguments for the fact that two α values result from Fischer–Tropsch synthesis occurring via two different mechanisms were presented later on [10, 12]. This also follows from the fact that either oxygen-containing compounds obtained from methanol [2] or methylene groups formed by the thermal decomposition of diazomethane [4] can be monocarbon units that participate in chain growth.

Previously [12], based on the concept of the C–C bond chain growth simultaneously through two types of

[1] Strictly speaking, this does not result in the equality of the rate constants of all steps of chain propagation (and all termination steps) regardless of the chain length, as is usually postulated (see review [1] and references cited therein). However, in the majority of publications, the authors consider expressions containing a ratio between the rate constants of chain propagation and termination rather than individual constants. In this case, the final result is the same when starting from the above postulate or accepting that the rate constants depend on n. However, when the rate constant of a chain-termination step changes, the rate constant of chain propagation changes by the same factor.

intermediates and a more detailed analysis of the MMD of the resulting hydrocarbons, the following mechanism of Fischer–Tropsch synthesis on the $Co/SiO_2 \cdot Zr(IV)$ catalyst was proposed:



(II)

where C_n are reaction products containing n carbon atoms; A_n and B_n are the surface intermediates of different types; $w'_{pr,n}$, $w''_{pr,n}$, $w'_{term,n}$, and $w''_{term,n}$ are the rates of the corresponding steps of chain propagation and termination; w_2 is the rate of the formation of C_2 hydrocarbons; and w is the rate of the formation of C_{4+} hydrocarbons by ethylene dimerization. Chain growth in scheme (II) occurs by the successive addition of monocarbon units to the intermediates A_n and B_n. In this scheme, the rates of hydrocarbon formation (w_n) for $n = 1$ and $n \geq 3$ are equal to the sum of the rates of chain termination ($w'_{term,n} + w''_{term,n}$), whereas

$$w_2 = w'_{term,2} + w''_{term,2} - 2w. \quad (8)$$

The aim of this work was to develop a mathematical model that describes the MMD of hydrocarbons formed according to scheme (II).

As the first stage, let us formulate an intermediate mathematical model to describe the MMD of C_{2+} hydrocarbons (hydrocarbons with $n \geq 2$) formed in accordance with scheme (II).

The MMD of hydrocarbons formed simultaneously via two different mechanisms can be described by the Huff–Sutterfield equation, which was initially proposed for the two-centered model containing three parameters α_1, α_2, and x [9]. When the initiation rate of C–C chain growth on the intermediates A_n is designated by w'_0, and that on the intermediates B_n is designated by w''_0, we have the following parameter:

$$x = \frac{w'_0}{w'_0 + w''_0}. \quad (9)$$

In order to describe the MMD of C_{2+} hydrocarbons formed via scheme (II), we have to introduce one more parameter, $-\gamma$, which is equal to the ratio of the amount of C_{4+} hydrocarbons formed by ethylene dimerization to the amount of the same products formed from the intermediates A_3.

$$\gamma = \frac{w}{w'_{pr,3}} = \frac{w}{\alpha_1^2 w'_{pr,1}}. \quad (10)$$

Using scheme (II) and Eqs. (7a), (7b), (8), and (10), we obtain the following expressions for the rates of hydrocarbon formation:

$$w_2 = (1-\alpha_1)w'_{pr,1} + (1-\alpha_2)w''_{pr,1} - 2w, \quad (11a)$$

$$w_3 = (1-\alpha_1)\alpha_1 w'_{pr,1} + (1-\alpha_2)\alpha_2 w''_{pr,1}, \quad (11b)$$

$$w_n = (1-\alpha_1)\alpha_1^{n-2}(1+\gamma)w'_{pr,1} + (1-\alpha_2)\alpha_2^{n-2}w''_{pr,1}. \quad (11c)$$

In Eq. (11c), $n \geq 4$.

By analogy with [9], we may introduce the parameter x, which can be presented, in this case, as the following expression:

$$x = \frac{w'_{pr,1}}{w'_{pr,1} + w''_{pr,1}} = \frac{w'_{pr,1}}{w_{2+} + w},$$

and, for brevity, the designation $A = \dfrac{1}{1-\alpha_1^2\gamma x}$. After the division of expressions (11a)–(11c) into w_{2+} (the overall rate of C_{2+} hydrocarbon formation), we obtain the system of MMD equations for higher hydrocarbons

$$m_2 = A[(1-\alpha_1)x + (1-\alpha_2)(1-x) - 2\gamma x\alpha_1^2], \quad (12a)$$

$$m_3 = A[(1-\alpha_1)\alpha_1 x + (1-\alpha_2)\alpha_2(1-x)], \quad (12b)$$

$$m_n = A[(1-\alpha_1)\alpha_1^{n-2}(1+\gamma)x + (1-\alpha_2)\alpha_2^{n-2}(1-x)], \quad (12c)$$

where $n \geq 4$.

The adequacy of the developed model was tested by experimental data obtained in CO hydrogenation (H_2 : CO = 2.5 ± 0.1) on the $Co/SiO_2Zr(IV)$ catalyst

Table 1. Experimental rates of hydrocarbon formation

$w_n \times 10^7$, mol g^{-1} s^{-1}	Experiment no.			
	1	2	3	4
w_1	10.630	3.454	4.351	48.491
w_2	2.518	1.077	1.539	2.214
w_3	3.303	1.343	1.980	1.605
w_4	2.996	1.228	1.789	1.267
w_5	1.057	0.492	0.594	0.452
w_6	0.482	0.274	0.323	0.265
w_7	0.213	0.138	0.258	0.125
w_8	0.095	0.080	0.112	0.092
w_9	0.043	0.032	0.041	0.092
w_{10}	0.030	0.019	0.030	0.080
w_{11}	0.026	0.017	0.026	0.069
w_{12}	0.023	0.016	0.022	0.059
w_{13}	0.023	0.016	0.019	0.050
w_{14}	0.021	0.016	0.016	0.043
w_{15}	0.018	0.012	0.012	0.037
w_{16}	0.015	0.009	0.008	0.033
w_{17+}	0.020	0.020	0.020	0.085

Table 2. MMD parameters calculated using Eqs. (12a)–(12c)

Experiment no.	MMD parameters of $C_{2+}(C_{4+})$* hydrocarbons			
	α_1	α_2	x	γ
1	0.382 (0.381)	0.941 (0.943)	0.952	1.483
2	0.449 (0.445)	0.938 (0.946)	0.927	0.908
3	0.441 (0.442)	0.858 (0.858)	0.927	0.939
4	0.313 (0.301)	0.879 (0.876)	0.777	1.782

* The MMD parameters calculated by the published method [8, 11] for the MMD of C_{4+} hydrocarbons.

containing 5 wt % Co and 1 wt % Zr under different conditions, namely,

Experiment no.	T, K	P, MPa	Space velocity of synthesis gas, h^{-1}
1	530	5	1350
2	530	2.5	620
3	510	5	1090
4	510	5	1440

Experiments 1, 2, and 3 were carried out after operating the catalyst for at least four days when the rates of formation of all products remained unchanged in time. Experiment 4 was conducted in a quasi-steady state after operating the catalyst for 10 h with an experiment duration of 4 h. The results of the experiments are presented in Table 1.

In all cases, the proposed mathematical model adequately describes the MMD of C_{2+} hydrocarbons. Table 2 contains the MMD parameters calculated by Eqs. (12a)–(12c). It is clear from the table that the probabilities of chain growth α_1 and α_2 calculated using these equations and the method proposed previously [8, 11] on the basis of the MMD of C_{4+} hydrocarbons are close: in most cases, a difference in the parameters can be found only in the third decimal digit. However, the calculated rates of methane formation $w'_{\text{term, 1}} + w''_{\text{term, 1}}$ determined from the values of $w'_{\text{pr, 1}}$, $w''_{\text{pr, 1}}$, α_1, and α_2 do not coincide with the experimental rates of methane formation (Tables 1 and 3). This can most likely be explained by the distinction between the mechanisms of the chain termination steps in the formation of methane and higher hydrocarbons.

Chain growth on the $Co/SiO_2Zr(IV)$ catalyst due to the addition of methylene groups (according to a polymerization mechanism) occurs with a lower α value, whereas chain growth through oxygen-containing structures (according to a hydrocondensation mechanism) occurs with a higher α value (through the intermediates A_n and B_n, respectively) [12]. In the former case, chain termination occurs with the formation of terminal olefins as primary products [13]. However, this mechanism of chain termination does not result in the formation of methane, which results from the hydrogenation of methyl groups [14]. Therefore, the probabilities of chain growth for the intermediate A_1 (α_1^{I}) and intermediates A_n at $n \geq 2$ (α_1) can differ.

Taking into account this fact, we can obtain the MMD equation for all hydrocarbons formed in Fischer–Tropsch synthesis on the $Co/SiO_2Zr(IV)$ catalyst.

The MMD of all hydrocarbons formed according to scheme (II) can be described by the equations containing the parameters α_1 and α_2

$$x = \frac{w_0'}{w_0' + w_0''} = \frac{w_0'}{w_0 + w}, \quad (13)$$

$$\gamma = \frac{w}{w_{pr,3}'} = \frac{w}{\omega\alpha_1^3 w_0'}, \quad (14)$$

$$\omega = \frac{\alpha_1^I}{\alpha_1}, \quad (15)$$

where ω is the parameter that takes into account the difference in the probabilities of chain growth for the intermediates A_1 and A_n at $n \geq 2$, and w_0 is the overall rate of hydrocarbon formation.

Based on scheme (II), the chain termination rates via two mechanisms with the formation of hydrocarbons containing different numbers of carbon atoms may be expressed as follows:

$$w_{term,1}' + w_{term,1}'' = (1 - \omega\alpha_1)w_0' + (1 - \alpha_2)w_0'', \quad (16a)$$

$$w_{term,2}' + w_{term,2}'' = (1 - \alpha_1)\omega\alpha_1 w_0' + (1 - \alpha_2)\alpha_2 w_0'', \quad (16b)$$

$$w_{term,3}' + w_{term,3}'' = (1 - \alpha_1)\omega\alpha_1^2 w_0' + (1 - \alpha_2)\alpha_2^2 w_0'', \quad (16c)$$

$$w_{term,n}' + w_{term,n}'' = (1 - \alpha_1)\omega\alpha_1^{n-1}(1 + \gamma)w_0' + (1 - \alpha_2)\alpha_2^{n-1}w_0''. \quad (16d)$$

In Eq. (16d), $n \geq 4$.

After dividing Eqs. (16) into the overall rate of hydrocarbon formation $w_0 = w_0' + w_0'' - w$, taking into account Eqs. (8) and (13)–(15) and introducing the designation $B = \frac{1}{1 - \alpha_1^3\omega\gamma x}$, we obtain

$$m_1 = B[(1 - \omega\alpha_1)x + (1 - \alpha_2)(1 - x)], \quad (17a)$$

$$m_2 = B[(1 - \omega\alpha_1)x\alpha_1 + (1 - \alpha_2)(1 - x)\alpha_2 - 2\omega\gamma x\alpha_1^3], \quad (17b)$$

$$m_3 = B[(1 - \omega\alpha_1)\alpha_1^2 x + (1 - \alpha_2)\alpha_2^2(1 - x)], \quad (17c)$$

$$m_n = B[(1 - \alpha_1)\omega\alpha_1^{n-1}(1 + \gamma)x + (1 - \alpha_2)\alpha_2^{n-1}(1 - x)], \quad (17d)$$

where $n \geq 4$.

In all cases, the molecular mass distributions of C_1–C_{16} hydrocarbons are well described by Eqs. (17a)–(17d) with the parameters presented in Table 4. Examples of the MMD for experiments 1 and 4 are presented in the figure. The mole fractions of C_{17+} hydrocarbons are underestimated due to experimental errors; the reasons for this have been repeatedly discussed in the literature [1, 10, 11, 15].

Equations (17a)–(17d) take into account the following three most abundant deviations from the ASF distribution [1]:

(1) The deviation in the C_1 region, which is explained by the distinction in the mechanisms of chain termination steps with the formation of methane and higher hydrocarbons in the C–C chain growth through the intermediates A_n and is taken into account by the ω parameter. Previously [16], it was found that the

Table 3. Calculated rates of methane formation

$w \times 10^7$, mol g^{-1} s^{-1}	Calculation method	Experiment no.			
		1	2	3	4
w_{2+} (experimental values)	–	10.89	4.79	6.79	6.57
$w_{pr,1}'$	$\frac{xw_{2+}}{1 - x\gamma\alpha_1^2}$	13.06	5.35	7.58	5.91
$w_{pr,1}''$	$\frac{w_{pr,1}'(1 - x)}{x}$	0.66	0.42	0.60	1.70
$w_{term,1}'$	$\frac{w_{pr,1}'(1 - \alpha_1)}{\alpha_1}$	21.12	6.56	9.60	12.96
$w_{term,1}''$	$\frac{w_{pr,1}''(1 - \alpha_2)}{\alpha_2}$	0.04	0.03	0.10	0.23
Calculated rates of methane formation	$w_{term,1}' + w_{term,1}''$	21.16	6.59	9.70	13.19

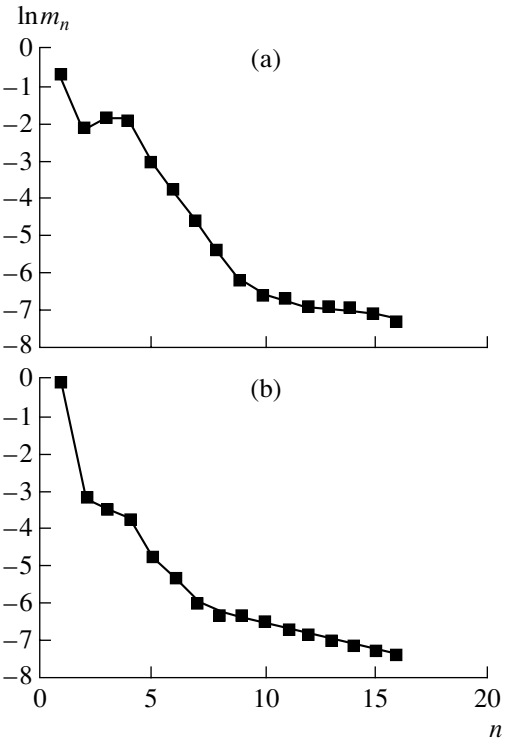


Fig. 1. Molecular mass distribution of hydrocarbons: (a) experiment 1 (T = 530 K, P = 5 MPa, space velocity of synthesis gas 1350 h^{-1}); (b) experiment 4 (T = 510 K, P = 5 MPa, space velocity of synthesis gas 1440 h^{-1}).

hydrogenating ability of the $Co/SiO_2Zr(IV)$ catalyst decreased during its operation. In terms of the above considerations, this should decrease the hydrogenation rate of methyl groups with methane formation. The latter is probably a reason for higher ω values on the catalyst that worked for some time as compared to the value obtained in the initial period of an experiment (Table 4).

(2) The deviation in the C_2 region is due to the secondary reaction of ethylene dimerization. At the same values of other parameters, the higher the γ, the more pronounced the deviation in the C_2 region. The same reaction can be responsible for the underestimated content of C_3 hydrocarbons. This is also a frequently occurring type of deviation [1].

Table 4. MMD parameters calculated using Eqs. (17a)–(17d)

Experiment no.	MMD parameters of C_{1+} hydrocarbons				
	α_1	α_2	x	γ	ω
1	0.380	0.943	0.971	1.500	1.479
2	0.447	0.943	0.951	0.919	1.406
3	0.441	0.858	0.945	0.938	1.449
4	0.312	0.879	0.966	1.779	0.359

(3) The nonlinearity of the MMD, which is explained by two different mechanisms of C–C bond chain growth, polymerization and hydrocondensation mechanisms. At x = 0 and x = 1, where the C–C bond chain grows only via one of the mechanisms, the MMD becomes linear.

Note that the proposed MMD equations ignore the destructive hydrogenation of ethylene, which can occur in the presence of some cobalt catalysts [17, 18], but apparently this does not play a significant role in Fischer–Tropsch synthesis on the $Co/SiO_2Zr(IV)$ catalyst.

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