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Partial Oxidation of Methane to Synthesis Gas over $NdCaCoO_4$ Catalyst: Kinetic Modeling of Autothermal Reforming

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Abstract—Partial oxidation of methane to synthesis gas using a highly selective catalyst based on $NdCaCoO_4$ has been studied, and rate constants have been determined. To determine the kinetic constants in a thin bed of the catalyst with a mass of 0.1 g, a model of isothermal syngas production process has been implemented and objective functions and computational algorithm to minimize the mismatch criterion between calculated and experimental data have been selected. The oxidative methane reforming process has been modeled in the isothermal and autothermal modes. The calculation results for the isothermal mode have been found to agree with experimental data.

Keywords: synthesis gas, methane conversion, catalyst, kinetic modeling

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Improvement in energy and resource efficiency of petrochemical plants is impossible without a thorough study and analysis of reactor processes, which usually occur in heterogeneous catalytic reactors. Solving these problems requires kinetic simulation of the reactor processes, which makes it possible to take into account the effect of main physicochemical and technological parameters of industrial production, primarily, the influence of the type of the catalyst used for the purpose. By applying kinetic models and kinetic simulation results, the reactor process scaling problems are solved, so the models can be widely used in the design of pilot, industrial pilot, and full-scale industrial units [1].

In performing the kinetic modeling of catalytic reactor processes, it is necessary to solve a set of problems, of which the main problem is to determine the parameters of a kinetic model, both structural parameters associated with the reaction mechanism and parametric characteristics, in particular, the rate constants of the relevant reactions. The determination of the kinetic constants of chemical reactions of basic organic and petrochemical synthesis is quite an important current task due to the variety of options for experimental investigation aiming to find these quantities; novel, more perfect and advanced hardware design of laboratory equipment; and development of new catalysts [2].

The procedure for solving the problem of determining the kinetic constants in an adiabatic batch reactor is described in [3, 4]. This procedure, used to determine the kinetic constants of liquid-phase reactions in terms of the perfect mixing model, is inapplicable to determination of the kinetic constants of gas-phase (or vapor phase) heterogeneous catalytic reactions, in which the plug-flow model should be used to describe the motion of flow.

The kinetic aspects of chemical reactions on various catalysts were studied in [2, 5–10].

A catalyst based on the perovskite-like material $NdCaCoO_4$ showed high performance and stability in partial oxidation of methane to synthesis gas; the selectivity to synthesis gas reached 100% at a methane conversion over 90% [11–13]. Thus, determining the kinetic constants of the syngas production process by the reaction with oxygen on this catalyst is a quite important task.

The solution of problems of parametric identification of gas-phase heterogeneous catalytic reactions using the plug-flow model is fraught with the following problems: selection of the identification criterion (data mismatch criterion which measures the discrepancy of experimental data from the model), choice of the algorithm and parameters for solving the system of differential equations taking into account the need to apply in some cases special algorithms for solving stiff

Table 1. Results of experiments on the oxidative conversion of methane over an $NdCaCoO_4$ catalyst in a laboratory reactor*

No.	β	W, mL/g/h	T, °C	$x_{CH_4}^{exp}$, %**	Y^{exp}, %		
					H_2	CO	CO_2
1	1.8	22500	889	79	59	62	17
2	1.8	22500	909	86	71	71	15
3	1.9	24107	910	93	82	85	8
4	1.9	21774	855	68	52	52	16
5	1.9	21774	885	88	80	77	11
6	2.4	20225	869	76	77	74	2
7	2.8	19708	871	84	70	82	2
8	2.9	19565	892	87	73	86	1
9	2.7	19355	872	90	71	89	1
10	2.5	19926	865	85	83	85	1
11	2.8	19636	893	79	77	78	1
12	2.7	19708	911	85	81	85	0
13	2.5	20074	923	74	68	72	2
14	2.6	20074	936	77	74	75	2
15	2.6	20074	957	78	75	77	1

* Determination errors for W, 2 mL/g/h; $T = 0.5$°C; and $x_{CH_4}^{exp}$ and product yield, 3 abs. %.

** The equilibrium conversion of methane under these experimental conditions is 100%.

systems of differential equations [14, 15], and choice of nonlinear programming methods for finding the minimum of the identification criterion [16].

These tasks require investigation and implementation of a method for modeling gas-phase heterogeneous catalytic processes in a plug-flow reactor.

The criterion of mismatch between calculated and experimental data is defined as follows [16]:

$$S = \int_0^L \sum_{u=1}^{V} \sum_{i=1}^{z} [y_i^{calc}(l) - y_i^{exp}(l)]^2 dl, \quad (1)$$

where y is the concentration of the components at the reactor outlet, the conversion of the principal reactant, or the selectivity and l is the reactor length.

As comparative physical quantities, both direct and indirect calculated and experimental data are used (example of the direct calculated data is the outlet concentrations of the components, and that of the indirect data is the conversion of the principal reactant or the product selectivity).

The objective of this study was to determine the kinetic constants of methane to syngas conversion by reaction with oxygen in an isothermal laboratory reactor using a catalyst based on $NdCaCoO_4$ to simulate the kinetics of this process run in the autothermal mode in laboratory and pilot reactors.

EXPERIMENTAL

Partial oxidation of methane to synthesis gas was investigated using a laboratory flow unit with a differential flow quartz reactor described in [11–13]. The catalyst charge loaded in the reactor was 0.1 g. The particle size of the catalyst was 0.51 mm, and the height of the catalyst bed was about 1 mm.

Analysis of the gas feed stream and the gaseous reaction products after establishing a constant temperature in the catalyst bed was performed using gas chromatography on a GALS-311 chromatograph with a thermal conductivity detector.

The results of experiments on the oxidative conversion of methane in the presence of the $NdCaCoO_4$ catalyst in the laboratory reactor are given in Table 1.

RESULTS AND DISCUSSION

Determination of Kinetic Constants of Oxygen Methane Reforming to Synthesis Gas

Basic assumptions:

(1) Chemical reactions occur according to the following scheme [17–21]:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (2)$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (3)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2. \quad (4)$$

(2) An examination of the literature shows that for adequate description of experimental kinetic data by regression analysis methods, it is suffice to use the equation $r_j = k_j \prod_{u=1}^{z-s} c_u$ [22]. For gas-phase reactions (2)–(4), we assumed that the rates of the steps are described by the equation $r_j = k_i p_{\text{react1}} p_{\text{react2}}$; $j = 1, 2, \ldots, w$; $k_4 = k_3 = k$; and $k_2 = ak$. The temperature dependence of the rate constants in this case is described by the equation $k = e^{A-\frac{B}{T}}$ (a, A, and B are the kinetic constants of reactions (2)–(4) and T is the absolute temperature).

(3) Methane combustion ceases when the mole fraction of oxygen becomes 0.002.

(4) Partial pressures of the components obey Dalton's law.

It is also assumed that when the first step of the process, the combustion of methane (reaction (2)), proceeds until the complete consumption of oxygen, reactions (3) and (4) can be ignored. Since the above reactions are heterogeneous catalytic, it is reasonable to write down the differential equations for the molar consumption rate of the components with respect to the mass of the catalyst [23]:

$$\frac{dn_{CH_4}}{dm_{\text{cat}}} = -k_2 p_{CH_4} p_{O_2}; \tag{5}$$

$$\frac{dn_{CO_2}}{dm_{\text{cat}}} = k_2 p_{CH_4} p_{O_2}; \tag{6}$$

$$\frac{dn_{O_2}}{dm_{\text{cat}}} = -2k_2 p_{CH_4} p_{O_2}; \tag{7}$$

$$\frac{dn_{H_2O}}{dm_{\text{cat}}} = 2k_2 p_{CH_4} p_{O_2}. \tag{8}$$

The system of ordinary differential equations (5)–(8) is complemented by the initial conditions:

$$n_{CH_4}(0) = n_{CH_4}^{(0)};\quad n_{CO_2}(0) = n_{CO_2}^{(0)};\quad n_{CO}(0) = n_{CO}^{(0)};$$
$$n_{H_2}(0) = n_{H_2}^{(0)};\quad n_{O_2}(0) = n_{O_2}^{(0)};\quad n_{H_2O}(0) = n_{H_2O}^{(0)}; N(0) = N^{(0)}.$$

To solve a system of mathematical description equations, the fourth-order Runge–Kutta method is used [14, 15].

The calculated molar consumptions of the components on the ith area of the catalyst charge (where the methane combustion finished) are input data for program no. 2 (module 2).

After the exhaustion of oxygen, methane reforming reaction (3) and (4) occur.

$$\frac{dn_{CH_4}}{dm_{\text{cat}}} = -k(p_{CH_4} p_{CO_2} + k p_{CH_4} p_{H_2O}); \tag{9}$$

$$\frac{dn_{CO_2}}{dm_{\text{cat}}} = -k p_{CH_4} p_{CO_2}; \tag{10}$$

$$\frac{dn_{CO}}{dm_{\text{cat}}} = k(2p_{CH_4} p_{CO_2} + p_{CH_4} p_{H_2O}); \tag{11}$$

$$\frac{dn_{H_2}}{dm_{\text{cat}}} = k(2p_{CH_4} p_{CO_2} + 3p_{CH_4} p_{H_2O}); \tag{12}$$

$$\frac{dn_{H_2O}}{dm_{\text{cat}}} = -k p_{CH_4} p_{H_2O}; \tag{13}$$

$$N = n_{CH_4} + n_{CO_2} + n_{CO} + n_{H_2} + n_{O_2} + n_{H_2O}. \tag{14}$$

The system of ordinary differential equations (9)–(14) is complemented by the initial conditions (**I** denotes module no. **I**):

$$n_{CH_4}(0) = n_{CH_4}^{(I)};\quad n_{CO_2}(0) = n_{CO_2}^{(I)};$$
$$n_{CO}(0) = n_{CO}^{(I)};\quad n_{H_2}(0) = n_{H_2}^{(I)};\quad n_{O_2}(0) = n_{O_2}^{(I)};$$
$$n_{H_2O}(0) = n_{H_2O}^{(I)};\quad N(0) = N^{(I)}.$$

This system of mathematical equations is solved using the 4th-order Runge–Kutta method.

To determine the kinetic constants, the mismatch criteria are minimized:

– direct test

$$S_{\text{dir}} = \sum_{i=1}^{15} [(n_{CH_4}^{\text{calc}} - n_{CH_4}^{\text{exp}})^2 + (n_{CO}^{\text{calc}} - n_{CO}^{\text{exp}})^2 + (n_{CO_2}^{\text{calc}} - n_{CO_2}^{\text{exp}})^2 + (n_{H_2}^{\text{calc}} - n_{H_2}^{\text{exp}})^2], \tag{15}$$

– indirect test

$$S_{\text{indir}} = \sum_{i=1}^{15} [(x_{CH_4}^{\text{calc}} - x_{CH_4}^{\text{exp}})^2 + (Y_{CO}^{\text{calc}} - Y_{CO}^{\text{exp}})^2 + (Y_{CO_2}^{\text{calc}} - Y_{CO_2}^{\text{exp}})^2 + (Y_{H_2}^{\text{calc}} - Y_{H_2}^{\text{exp}})^2] \tag{16}$$

wherein the component consumption rates in Eq. (15) are to be taken in mmol/h. The yields of CO, CO_2, and H_2 are related to the molar consumption rates by the following expressions:

$$Y_{CO} = \frac{n_{CO}}{n_{CH_4}^{(0)}};\quad Y_{CO_2} = \frac{n_{CO_2}}{n_{CH_4}^{(0)}};\quad Y_{H_2} = \frac{n_{H_2}}{2n_{CH_4}^{(0)}}.$$

Experimental values for CH_4 conversion are taken from the table of experimental results (Table 1), as well as the experimental yields of CO, CO_2, and H_2. The procedure for determining the kinetic constants for gas-phase heterogeneous catalytic reactions is described in [24]. Analysis of the experimental data has shown that it is necessary to select the following interval of varying the kinetic constants: $A \in [-1; 2]$; $B \in [16000; 24000]$; $a \in [1; 9]$.

The kinetic constants were determined by finding the minimum in mismatch criteria (15) and (16) using the penalty function method [14, 15].

The determination of the three kinetic constants for reactions (2)–(4) was performed in the aforemen-

Table 2. Results of finding kinetic constants

No.		Constants			
		A	B	A	S
1	Initial value	–0.95	16500	1.01	86117
	Results of minimization of direct test	–0.98	16004	7.22	15035
	Minimization of indirect test	1.28	16574	1.75	6723
2	Initial value	1.95	23500	8.99	100219
	Results of minimization of direct test	–0.96	16000	9	15073
	Minimization of indirect test	2	17337	1.27	6631
3	Initial value	–0.95	23500	8.99	112656
	Results of minimization of direct test	–1	16007.3	8.80	15052
	Minimization of indirect test	0.89	16000	1	6599
4	Initial value	–0.95	16500	8.99	19815
	Results of minimization of direct test	–0.82	16000	3.63	15120
	Minimization of indirect test	2	17339	1.18	6601
5	Initial value	1.95	16500	1.05	50582
	Results of minimization of direct test	–0.78	16000	3.24	15203
	Minimization of indirect test	1.76	17075	1.18	6586

tioned intervals of their change; the results are given in Table 2.

Numerous computational studies showed that it is useful to include indirect calculated and experimental data (conversions of the main reactants and yields of certain products) in the mismatch criterion and minimize Eq. (16).

It was established that the following kinetic constants are the most appropriate for solving the problem of kinetic modeling of the oxygen methane reforming to syngas: $A = 1.76$, $B = 17075$, and $a = 1.18$ (indirect mismatch criterion $S = 6586$).

The results of the kinetic modeling of the syngas production process in the laboratory reactor under isothermal conditions (weight ratios of the components at the reactor outlet for experimental data point no. 6 in Table 1 are shown in Table 3).

Changes in component concentrations reduced to the catalyst weight, the so-called concentration profiles with the kinetic constants found, are illustrated in Fig. 1.

Investigation of the mathematical simulation method and the procedure for finding the kinetic constants showed satisfactory agreement, being consistent from the computational point of view and by coincidence of the calculated and experimental data.

Table 3. Comparison of the calculated properties of the laboratory reactor output stream (for experimental data point no. 6) as given in Table 1 with experimental values

Stream property	Value		
P, kPa	100		
t, °C	869		
G, g/h	1.87		
	At the inlet	At the outlet	
ω	calculated data	calculated data	experimental data
CH_4	0.55	0.14	0.13
CO_2	0	0.04	0.03
CO	0	0.69	0.71
H_2	0	0.1	0.11
O_2	0.45	0	0
H_2O	0	0.03	0.02
$x^{calc}_{CH_4}$, %	74.55		

Construction of a Kinetic Model for Methane-to-Syngas Conversion with Oxygen in the Autothermal Mode on a Thin Catalyst Bed

Since recently, resource problems in chemical and petrochemical industries are among the most important in chemical engineering; therefore, many processes are tried to be conducted in the autothermal mode when it is possible. Haldor Topsøe designed an autothermal syngas production process [25].

Kinetic modeling of this process is needed for its investigation aiming to include in a model flow chart of an experimental (laboratory, pilot, or industrial) syngas production unit during the preparation of input data for chemical engineering design projects. Note that the input data (temperature, pressure, and feed stream composition) for kinetic simulation of the process to occur in the autothermal mode should be as close as possible to actual industrial conditions. In solving this problem, it is necessary to take into account the heats of all of the reactions. The temperature at the inlet of the (laboratory or pilot) autothermal reactor must not exceed the ignition temperature of the methane–oxygen mixture.

Equations (5)–(8) are complemented by the heat balance equation. Heat balance on a thin catalyst bed can be defined in terms of the perfect mixing model [26]

$$N^{(0)}c_p^{(0)}T^{(0)} - Nc_{pI}^{\mathrm{cp}}T + M_{\mathrm{cat}}^{\mathrm{I}}\Delta q_{\mathrm{cpI}}^{R} + Q_{\mathrm{comb}} = 0, \qquad (17)$$

where $M^{\mathrm{I}}_{\mathrm{cat}}$ is the portion of the catalyst weight in which exothermic reaction (2) of methane combustion proceeds.

From the heat balance equation, the heat withdrawn from the zone of exothermic reaction (2) and transferred for occurrence of endothermic reactions (3) and (4) is determined. Heat losses through the reactor walls and along the walls are neglected.

Calculated temperature T in the reactor is determined by solving the heat balance equation for the methane conversion zone $N^{(0)}c_{p\mathrm{I}}^{\mathrm{av}}T - Nc_{p\mathrm{II}}^{\mathrm{av}}T + (M_{\mathrm{cat}} - M_{\mathrm{cat}}^{I})\Delta q_{\mathrm{cpII}}^{R} + Q_{\mathrm{II}} = 0$.

The algorithm for calculating autothermal processes on a thin catalyst bed and its implementation for calculating an experimental syngas production reactor are described in [27]. A solution to the problem of incorporation of the model oxygen methane reforming reactor into a model flow sheet of industrial syngas production is given in [28].

The results of the kinetic modeling of the process of syngas production by oxygen methane reforming with 0.1 g of the catalyst (laboratory reactor) and 1000 g of the catalyst (pilot reactor) are presented in Tables 4 and 5, respectively (note that the weight fractions at the reactor outlet are calculated values). Figures 2 and 3 show the relevant concentration profiles.

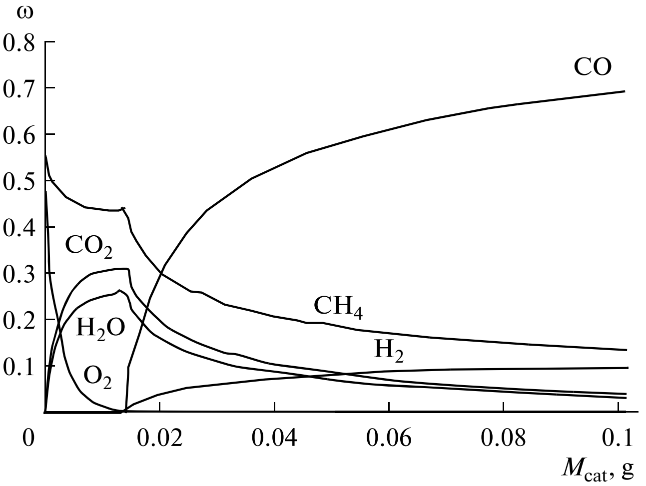

Fig. 1. Change in the weight fractions of the components along the reactor length (per unit weight of catalyst) for experimental data point no. 6 in Table 1.

Comparison of the calculation results on the laboratory reactor operating in the isothermal mode (Table 3 and Fig. 1) with the calculation results for the autothermal laboratory and pilot reactors (Tables 4, 5; Figs. 2, 3) showed that the methane conversion and the design temperature in the autothermal mode are lower than the conversion and the tabulated temperature (Table 1) in the isothermal laboratory reactor. The difference is due to the fact that the inlet temperature of the autothermal reactor (laboratory or pilot) is below the temperature at the inlet of the isothermal laboratory reactor (in experiments on laboratory reactor, temperature is measured only in the catalyst bed, which is placed in an electric furnace), which is associated with the fact that the temperature at the reactor inlet of the laboratory, pilot, or industrial unit may not exceed the ignition temperature of the methane–oxygen mixture (ignition temperature of the methane–oxygen mixture is in the range of 537–545°C) [29]. The latter circumstance is important in the development of a model of an experimental (laboratory, pilot,

Table 4. Results of kinetic modeling of the methane to syngas conversion process by oxygen reforming (0.1 g of catalyst. laboratory reactor)

Stream property		
P, kPa	100	
$t^{(0)}$, °C	489	
t^{calc}, °C	827	
G, g/h	1.87	
ω	at the inlet	at the outlet
CH_4	0.55	0.21
CO_2	0	0.11
CO	0	0.52
H_2	0	0.08
O_2	0.45	0
H_2O	0	0.08
Q_{comb}, J/h	–7.27	
$x_{CH_4}^{\mathrm{calc}}$, %	61.82	

Table 5. Results of kinetic modeling of the methane to syngas conversion process by oxygen reforming with a catalyst charge of 1000 g (pilot reactor)

Stream property		
P, kPa	100	
$t^{(0)}$,°C	489	
t^{calc},°C	827	
G, g/h	17161	
ω	at the inlet	at the outlet
CH_4	0.55	0.21
CO_2	0	0.11
CO	0	0.52
H_2	0	0.08
O_2	0.45	0
H_2O	0	0.08
Q_{comb}, J/h	−77282	
$x^{calc}_{CH_4}$, %	61.82	

or commercial) syngas production flow sheet in the preparation of the input data upon designing of chemical plants.

In summary, the kinetic constants of the process for syngas production by oxygen methane reforming in the presence of an $NdCaCoO_4$ catalyst have been determined. The isothermal and autothermal modes of the process in a laboratory reactor with 0.1 g of catalyst charge and a pilot reactor with 1000 g of catalyst have been kinetically modeled.

The characteristic features of the proposed method of identification are (1) quasi-homogeneous description of the processes on the catalyst; (2) in the simulated process of autothermal oxidative methane conversion, the temperature in the exothermic reaction zone is equal to that in the zone of endothermic reactions, which is possible because of the thin bed of the catalyst; (3) the heat withdrawn from the exothermic reaction zone is completely transferred to the zone of endothermic reactions; and (4) component-by-component balance equations of mathematical description in the areas of the exothermic reaction and endothermic reactions are defined in terms of plug-flow models, and heat balance equations are defined by perfect mixing models.

The comparison of the results of the computational study revealed that trends in component concentrations referred to the catalyst weight for the laboratory and pilot reactors operating in the autothermal mode are the same as those for the isothermal laboratory reactor.

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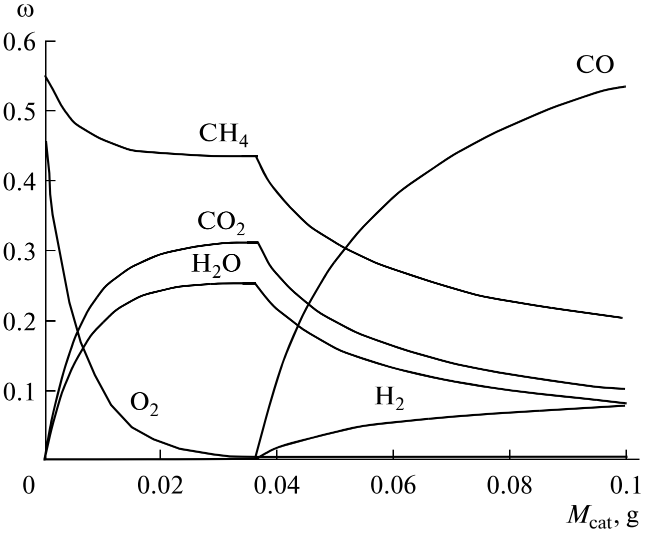

Fig. 2. Change in the weight fractions of the components along the reactor length (catalyst weight of 0.1 g, laboratory reactor).

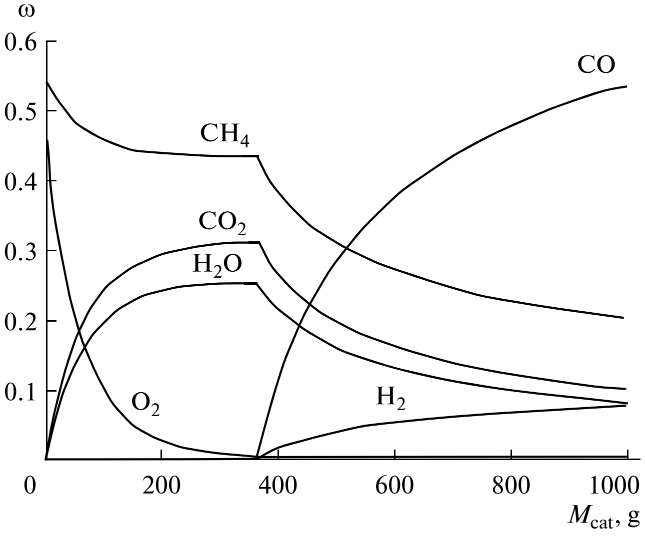

Fig. 3. Change in the weight fractions of the components along the reactor length (catalyst weight of 1000 g, pilot reactor).

SYMBOLS

In determining the kinetic constants and mathematical modeling, we used the following symbols:

a, A, and *B*—kinetic constants (coefficients of rate equations); ß—methane/oxygen molar ratio; c_p—heat capacity, kJ/(kmol K); *G*—mass flow, g/h or kg/h; *g*—local space velocity of the component in the stream, kmol/(g cat h); *k*—the rate reaction constant, 1/(kPa h); *l*—reactor length, m; *m*—the coordinate of the catalyst mass; *M*—catalyst mass, g; *N*—total molar flow rate, kmol/h; *n*—component molar flow rate, mmol/h, mol/h, or kmol/h; *P*—partial pressure in kPa; *Q*—heat flux, J/h or kJ/h; *S*—mismatch criterion; *T*—temperature, K; *t*—temperature, °C; *r*—reaction rate, kmol/(g cat h); *x*—conversion,%; *Y*—yield, %; *W*—feed hourly space velocity per gram of catalyst, mL/(g cat h); *w*—number of reactions; Δq—local intensity of heat source, kJ/(g cat h); and ω—mass fraction of component.

Subscripts/superscripts: (0)—initial value at the inlet, I—zone of exothermic reactions, II—zone of endothermic reactions, *i*—component number, *j*—step number, *cat*—catalyst, *z*—number of components, *s*—number of reactants, *u*—reactant number, *v*—number of data points, *w*—number of reactions, R—reaction, indir—indirect, dir—direct, calc—calculated value, exp—experimental value.

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