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# Kinetic Simulation of the Oxidative Condensation of Methane

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**Abstract**—The kinetics of the oxidative condensation of methane (OCM) over a mixed-oxide lithium–manganese–tungsten–silicate catalyst has been simulated, and systems of stoichiometric chemical equations possible under the OCM conditions have thereby been discriminated. A phenomenological kinetic model has been developed to fit the observed rates of formation and disappearance of the compounds involved in OCM.

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The oxidative conversion of methane (OCM) has been attracting researchers' attention all over the world for more than 30 years. It is among the promising processes for obtaining petrochemical synthesis products from natural gas, an alternative raw material. There have been many publications suggesting various catalysts and process conditions for OCM [1, 2].

A specific feature of OCM is that it needs high temperatures and is comparatively low-selective. Because of the high process temperature, OCM yields not only ethane and ethylene, but also a number of by-products, such as carbon monoxide and dioxide, water, and hydrogen. Although new, more selective composite oxide catalysts based on silicon, tungsten, and manganese have been proposed in recent years [3–8], the role of side reactions still remains significant [9].

The kinetics of OCM has been the subject of numerous studies [10–25]; however, the detailed mechanism of this reaction is still a matter of controversy. In view of this, most authors rely on phenomenological kinetic models [9, 26–33]. In our earlier work on the kinetics of OCM over lanthanum–cerium catalysts [33], we suggested phenomenological model (1), in which the OCM kinetics is approximated by the system of stoichiometric equations (I):

$$
\begin{aligned}
\frac{\mathrm{d}y_{\mathrm{CH_4}}}{\mathrm{d}\tau} &= -4k_1P^3C_{\mathrm{CH_4}}C_{\mathrm{O_2}} - k_4P^2C_{\mathrm{CH_4}}C_{\mathrm{O_2}} - 2k_7P^2C_{\mathrm{CH_4}}C_{\mathrm{O_2}},\\
\frac{\mathrm{d}y_{\mathrm{O_2}}}{\mathrm{d}\tau} &= -k_1P^3C_{\mathrm{CH_4}}C_{\mathrm{O_2}} - k_2P^2C_{\mathrm{O_2}}C_{\mathrm{C_2H_6}} - 2k_3P^2C_{\mathrm{C_2H_4}}C_{\mathrm{O_2}} - 2k_4P^2C_{\mathrm{O_2}}C_{\mathrm{CH_4}}\\
&\quad - 3k_6P^2C_{\mathrm{O_2}}C_{\mathrm{C_2H_4}} - k_7P^2C_{\mathrm{C_2H_4}}C_{\mathrm{O_2}} - 0.5k_8P^{2.583}C_{\mathrm{CH_4}}^{1.86}C_{\mathrm{O_2}}^{0.723},\\
\frac{\mathrm{d}y_{\mathrm{C_2H_4}}}{\mathrm{d}\tau} &= 2k_2P^2C_{\mathrm{O_2}}C_{\mathrm{C_2H_6}} - k_3P^2C_{\mathrm{O_2}}C_{\mathrm{C_2H_4}} - k_6P^2C_{\mathrm{O_2}}C_{\mathrm{C_2H_4}} - 2k_8P^{2.583}C_{\mathrm{CH_4}}^{1.86}C_{\mathrm{O_2}}^{0.723},\\
\frac{\mathrm{d}y_{\mathrm{C_2H_6}}}{\mathrm{d}\tau} &= 2k_1P^2C_{\mathrm{CH_4}}C_{\mathrm{O_2}} - 2k_2P^2C_{\mathrm{O_2}}C_{\mathrm{C_2H_6}} - k_8P^{2.583}C_{\mathrm{CH_4}}^{1.86}C_{\mathrm{O_2}}^{0.723},\\
\frac{\mathrm{d}y_{\mathrm{C_3H_6}}}{\mathrm{d}\tau} &= 2k_8P^{2.583}C_{\mathrm{CH_4}}^{1.86}C_{\mathrm{O_2}}^{0.723},\\
\frac{\mathrm{d}y_{\mathrm{CO_2}}}{\mathrm{d}\tau} &= k_4P^2C_{\mathrm{O_2}}C_{\mathrm{CH_4}} - k_5P^2C_{\mathrm{CO_2}}C_{\mathrm{H_2}} + \frac{k_5}{K_p}P^2C_{\mathrm{CO}}C_{\mathrm{H_2O}} + 2k_6P^2C_{\mathrm{C_2H_4}}C_{\mathrm{O_2}},\\
\frac{\mathrm{d}y_{\mathrm{CO}}}{\mathrm{d}\tau} &= 2k_3P^2C_{\mathrm{O_2}}C_{\mathrm{C_2H_4}} + k_5P^2C_{\mathrm{CO_2}}C_{\mathrm{H_2}} - \frac{k_5}{K_p}P^2C_{\mathrm{CO}}C_{\mathrm{H_2O}},\\
\frac{\mathrm{d}y_{\mathrm{H_2}}}{\mathrm{d}\tau} &= -k_5P^2C_{\mathrm{CO_2}}C_{\mathrm{H_2}} + \frac{k_5}{K_p}P^2C_{\mathrm{CO}}C_{\mathrm{H_2O}},\\
\frac{\mathrm{d}y_{\mathrm{H_2O}}}{\mathrm{d}\tau} &= 2k_1P^3C_{\mathrm{CH_4}}C_{\mathrm{O_2}} + 2k_2P^2C_{\mathrm{O_2}}C_{\mathrm{C_2H_6}} + 2k_3P^2C_{\mathrm{C_2H_4}}C_{\mathrm{O_2}} + 2k_4P^2C_{\mathrm{O_2}}C_{\mathrm{CH_4}} + k_5P^2C_{\mathrm{CO_2}}C_{\mathrm{H_2}}\\
&\quad - \frac{k_5}{K_p}P^2C_{\mathrm{CO}}C_{\mathrm{H_2O}} + 2k_6P^2C_{\mathrm{O_2}}C_{\mathrm{C_2H_4}} + 2k_7P^2C_{\mathrm{C_2H_4}}C_{\mathrm{O_2}} + k_8P^{2.583}C_{\mathrm{CH_4}}^{1.86}C_{\mathrm{O_2}}^{0.723},
\end{aligned}
\tag{1}
$$

where $\tau$ is the residence time, $y_i = W_i/W_0$ is the fraction of the $i$th component in the reaction stream ($W_0$ and $W_i$ are the total feed flow rate and $W_i$ is the flow rate of the $i$th component at the reactor inlet, respectively), $P$ is the total pressure in the system, $C_i = y_i / \sum_i y_i$ is the mole fraction of the $i$th component in the system, $k_j$ is the rate constant of the $j$th reaction, and $K_p$ is the equilibrium constant of the reversible reaction.

We used the same kinetic model and the same approximation to account for the kinetic data obtained with a $LiWMn/SiO_2$ catalyst [9].

| Step no. | System (I) [9] |
|---|---|
| 1 | $4CH_4 + O_2 \rightarrow 2C_2H_6 + 2H_2O$ |
| 2 | $2C_2H_6 + O_2 \rightarrow 2C_2H_4 + 2H_2O$ |
| 3 | $C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$ |
| 4 | $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ |
| 5 | $CO_2 + H_2 \leftrightarrow CO + H_2O$ |
| 6 | $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ |
| 7 | $2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$ |
| 8 | $C_2H_6 + 2C_2H_4 + 0.5O_2 \rightarrow 2C_3H_6 + H_2O$ |

Almost simultaneously with the appearance of our works, there were publications by other authors on the kinetics of OCM over similar catalysts [28, 34]. Shahri and Alavi [28] investigated the OCM kinetics on a $Mn/Na_2WO_4/SiO_2$ catalyst, varying the reaction temperature (800–900°C), methane : oxygen ratio (3.4–4.6), and residence time (85–345 kg s nm$^{-3}$ (STP)). It was demonstrated that extending the residence time and raising the temperature improve the process outcomes, while increasing the methane-to-oxygen ratio decreases the methane and oxygen conversions. Addition of ethane, ethylene, CO, and $CO_2$ to the feed reduces the product formation rate. A kinetic model of OCM based on the system of stoichiometric equations (II) was suggested [28]. In this model, the reaction rates are written as follows:

$$r_1 = \frac{k_{01}\exp(-E_{a,1}/RT)\,P_{CH_4}^{m1}P_{O_2}^{n1}}{\left(1 + K_{1,CH4}\exp(-\Delta H_{ad,1,CH_4}/RT)\,P_{CH_4} + K_{1,O_2}\exp(-\Delta H_{ad,1,O_2}/RT)\,P_{O_2}\right)^2},$$

$$r_j = \frac{k_{0j}\exp(-E_{a,j}/RT)\,P_C^{mj}P_{O_2}^{nj}}{\left(1 + K_{j,C}\exp(-\Delta H_{ad,j,C}/RT)\,P_C^{mj} + K_{j,O_2}\exp(-\Delta H_{ad,j,O_2}/RT)\,P_{O_2}^{nj}\right)^2}, \text{ where } j = 2, 3, 4, 6; \quad (2)$$

$$r_5 = k_{05}\exp(-E_{a,5}/RT)\,P_{CO_2}^{m5}P_{H_2}^{n5} - \frac{k_{05}}{K_p}\exp(-E_{a,5}/RT)\,P_{CO}^{m5}P_{H_2O}^{n5},$$

where $P_C$ is the partial pressure of the hydrocarbon involved in the $j$th reaction, $E_{a,j}$ is the activation energy of the $j$th reaction, $k_{0j}$ is the preexponential factor of the $j$th reaction, $\Delta H_{ad,j,O_2}$ is the enthalpy of adsorption of oxygen on the catalyst surface for the $j$th reaction, $K_{j,O_2}$ is the oxygen adsorption constant for the $j$th reaction, $\Delta H_{ad,j,C}$ is the enthalpy of adsorption of the hydrocarbon involved in the $j$th reaction on the catalyst surface, $K_{j,C}$ is the adsorption constant of the hydrocarbon involved in the $j$th reaction, $K_p$ is the equilibrium constant of the reversible reaction, $m_j$ and $n_j$ are the orders of the $j$th reaction, and $r_j$ is the rate of the $j$th reaction.

| Step no. | System (II) [28] |
|---|---|
| 1 | $4CH_4 + O_2 \rightarrow 2C_2H_6 + 2H_2O$ |
| 2 | $2C_2H_6 + O_2 \rightarrow 2C_2H_4 + 2H_2O$ |
| 3 | $C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$ |
| 4 | $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ |
| 5 | $CO_2 + H_2 \leftrightarrow CO + H_2O$ |
| 6 | $CH_4 + 1.5O_2 \rightarrow CO + 2H_2O$ |

| Step no. | System (III) [34] |
|---|---|
| 1 | $4CH_4 + O_2 \rightarrow 2C_2H_6 + 2H_2O$ |
| 2 | $2C_2H_6 + O_2 \rightarrow 2C_2H_4 + 2H_2O$ |
| 3 | $C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$ |
| 4 | $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ |
| 5 | $CO_2 + H_2 \leftrightarrow CO + H_2O$ |
| 6 | $CH_4 + O_2 \rightarrow CO + H_2O + H_2$ |
| 7 | $C_2H_6 \rightarrow C_2H_4 + H_2$ |
| 8 | $C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2$ |
| 9 | $2CO + O_2 \rightarrow 2CO_2$ |

The kinetics of OCM over a $Mn/Na_2WO_4/SiO_2$ catalyst at 750–875°C, methane : oxygen = 4.0–7.5, and a residence time of 30–160 kg s m$^{-3}$ (STP) was investigated by Daneshpayeh et al. [34]. It was demonstrated that, as the residence time is extended, the methane and oxygen conversions increase and the ethylene selectivity decreases. Raising the reaction temperature increases the methane conversion and ethylene selectivity and reduces the ethane selectivity. As the methane-to-oxygen ratio is increased, the ethane selectivity increases and the ethylene selectivity remains invariable. The reaction kinetics was described by the authors in terms of the model suggested earlier for a $La_2O_3/CaO$ catalyst [35]. This model is based on the system of stoichiometric equations (III):

$$r_1 = \frac{k_{01}\exp(-E_{a,1}/RT)\left(K_{0,O_2}\exp(-\Delta H_{ad,O_2}/RT)P_{O_2}\right)^{n1}P_{CH_4}^{m1}}{\left(1+\left(K_{0,O_2}\exp(-\Delta H_{ad,O_2}/RT)P_{O_2}\right)^{n1}\right)^2},$$

$$r_j = k_{0j}\exp(-E_{a,j}/RT)P_C^{mj}P_{O_2}^{nj}, \text{ where } j = 2, 3, 4, 6, 9,$$

$$r_5 = k_{05}\exp(-E_{a,5}/RT)P_{CO_2}^{m5}P_{H_2}^{n5} - \frac{k_{05}}{K_p}\exp(-E_{a,5}/RT)P_{CO}^{m5}P_{H_2O}^{n5}, \quad (3)$$

$$r_7 = k_{07}\exp(-E_{a,7}/RT)P_{C_2H_6},$$

$$r_8 = k_{08}\exp(-E_{a,8}/RT)P_{C_2H_4}^{m8}P_{H_2O}^{n8}.$$

Note that the above rate equations [28, 35] involve the heats of adsorption of methane, oxygen, $CO_2$, and carbon. According to the theory of complex reactions [36], use of the concept of the rate of the overall reaction (stoichiometric equation of a reaction pathway) in the kinetic description of a complex reaction makes sense only if there is a hypothesis as to the detailed mechanism of this reaction. If there is no such hypothesis, it is possible to take a phenomenological approach in which some reaction rate is assigned to each stoichiometric equation; however, only the rates with respect to particular compounds will have a physical meaning in this case. When several reactions take place, the rates of particular reactions cannot be measured by physical methods.

Note also that the cumbersome kinetic models suggested in [28, 35] involve tens of kinetic parameters. At the same time, it is known from the theory of solving inverse problems [37] that, when the number of parameters is so large as to be comparable with the number of experiments, some parameters may be correlated, and this would considerably devalue the model and would make the values of the fitted parameters less reliable. Because of the awkwardness of these kinetic models, it is difficult to distinguish their most significant properties.

Shahri and Alavi [28] used Fisher's and Student's tests to validate their phenomenological model. However, use of statistical tests needs some assumptions to be made. The most important of them is the linearity of the equations of the correlation model, whereas this is not the case for chemical kinetic equations.

Examination of stoichiometric equations (I)–(III) demonstrates that, in all of the reaction systems suggested, the OCM products form via the following reactions: ethane results from direct methane oxidation; ethylene, from the oxidative dehydrogenation of ethane; CO, from ethylene oxidation and from partial methane oxidation; $CO_2$, from total methane oxidation and from the water gas shift reaction; $H_2$, from the water gas shift reaction and from partial methane oxidation; $H_2O$, from hydrocarbon (methane, ethane, and ethylene) oxidation.

Reaction system (I), as distinct from (II) and (III), includes direct methane oxidation into ethylene and a $C_3$ hydrocarbon formation reaction. Reaction system (III) includes partial methane oxidation into CO, $H_2$, and $H_2O$; ethane dehydrogenation; and the steam ethylene reforming reaction.

The purpose of this work is to analyze and discriminate systems of stoichiometric reactions that can be involved in OCM.

## RESULTS AND DISCUSSION

An analysis of the above systems of overall chemical equations suggests that OCM can be described in terms of another system of stoichiometric equations (system (IV)). This system takes into account that ethane dehydrogenation into ethylene and steam ethane reforming can occur at high temperatures and excludes ethylene formation via direct methane oxidation as an unlikely reaction.

| Step no. | System (IV) |
|---|---|
| 1 | $4CH_4 + O_2 \rightarrow 2C_2H_6 + 2H_2O$ |
| 2 | $2C_2H_6 + O_2 \rightarrow 2C_2H_4 + 2H_2O$ |
| 3 | $C_2H_4 + 2O_2 \rightarrow 2CO + 2H_2O$ |
| 4 | $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ |
| 5 | $CO_2 + H_2 \leftrightarrow CO + H_2O$ |
| 6 | $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$ |
| 7 | $C_2H_6 \rightarrow C_2H_4 + H_2$ |
| 8 | $C_2H_6 + 2H_2O \rightarrow 2CO + 5H_2$ |

Thus, the above qualitative analysis demonstrated that four systems of stoichiometric chemical equations are possible, and, therefore, they need to be discriminated.

**Table 1.** Experimental kinetic data for the OCM process over the lithium–manganese catalyst

| $CH_4:O_2$ | $T$, °C | $W$, ml/h | Inlet flow rate, ml/h | | | Outlet flow rate, ml/h | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $CH_4$ | $O_2$ | $N_2$ | $H_2$ | $O_2$ | $N_2$ | CO | $CH_4$ | $CO_2$ | $C_2H_4$ | $C_2H_6$ | $C_3H_6$ | $C_3H_8$ | $C_4H_8$ |
| 2.00 | 857 | 2992 | 1938 | 969 | 85 | 0 | 55 | 85 | 286 | 1097 | 139 | 145 | 44 | 8 | 1 | 3 |
| 2.00 | 884 | 2960 | 1912 | 956 | 93 | 0 | 46 | 93 | 312 | 1093 | 130 | 135 | 37 | 7 | 1 | 3 |
| 2.00 | 911 | 2989 | 1934 | 967 | 89 | 0 | 32 | 89 | 321 | 1132 | 129 | 129 | 35 | 1 | 7 | 0 |
| 2.13 | 854 | 5910 | 3967 | 1862 | 81 | 1 | 141 | 81 | 574 | 2178 | 272 | 318 | 106 | 18 | 3 | 8 |
| 2.09 | 897 | 5809 | 3882 | 1857 | 70 | 0 | 51 | 70 | 641 | 2186 | 273 | 284 | 75 | 16 | 0 | 4 |
| 2.32 | 932 | 5739 | 3949 | 1702 | 88 | 0 | 42 | 88 | 663 | 2231 | 276 | 278 | 72 | 16 | 1 | 7 |
| 2.11 | 742 | 6038 | 3959 | 1876 | 203 | 0 | 1802 | 203 | 6 | 3884 | 9 | 6 | 24 | 0 | 0 | 0 |
| 1.98 | 801 | 5957 | 3851 | 1945 | 161 | 0 | 1641 | 161 | 37 | 3503 | 27 | 52 | 87 | 1 | 1 | 0 |
| 2.24 | 885 | 5672 | 3874 | 1729 | 69 | 1 | 111 | 69 | 600 | 2138 | 262 | 309 | 84 | 18 | 2 | 7 |
| 2.36 | 878 | 5944 | 4126 | 1748 | 70 | 0 | 123 | 70 | 503 | 2516 | 216 | 311 | 92 | 18 | 1 | 7 |
| 2.42 | 911 | 5901 | 4121 | 1703 | 77 | 0 | 70 | 77 | 545 | 2474 | 214 | 303 | 88 | 20 | 2 | 10 |
| 2.42 | 924 | 5925 | 4137 | 1710 | 78 | 0 | 56 | 78 | 572 | 2509 | 210 | 296 | 79 | 19 | 1 | 9 |
| 2.44 | 933 | 5812 | 4068 | 1667 | 77 | 1 | 45 | 77 | 579 | 2490 | 202 | 283 | 74 | 16 | 1 | 8 |
| 3.06 | 830 | 5866 | 4408 | 1441 | 17 | 0 | 1114 | 17 | 61 | 3771 | 35 | 114 | 124 | 5 | 2 | 11 |
| 3.18 | 897 | 5938 | 4463 | 1403 | 72 | 1 | 92 | 72 | 414 | 2967 | 163 | 313 | 108 | 18 | 1 | 5 |
| 3.18 | 926 | 5992 | 4499 | 1415 | 78 | 1 | 51 | 78 | 449 | 2993 | 152 | 306 | 96 | 17 | 2 | 11 |
| 3.06 | 944 | 5966 | 4436 | 1450 | 80 | 1 | 33 | 80 | 472 | 2979 | 158 | 289 | 86 | 19 | 0 | 5 |
| 3.60 | 827 | 6115 | 4770 | 1325 | 20 | 0 | 1002 | 20 | 41 | 4263 | 25 | 90 | 116 | 3 | 0 | 5 |
| 3.99 | 882 | 5791 | 4581 | 1148 | 62 | 1 | 134 | 62 | 277 | 3300 | 118 | 292 | 111 | 18 | 2 | 5 |
| 3.75 | 915 | 6119 | 4770 | 1272 | 77 | 1 | 65 | 77 | 343 | 3436 | 126 | 293 | 93 | 21 | 2 | 6 |
| 3.97 | 930 | 6042 | 4763 | 1200 | 79 | 1 | 47 | 79 | 358 | 3457 | 124 | 286 | 84 | 19 | 1 | 6 |
| 4.20 | 938 | 5914 | 4711 | 1122 | 81 | 1 | 42 | 81 | 372 | 3433 | 117 | 278 | 79 | 17 | 0 | 6 |
| 4.80 | 822 | 6029 | 4970 | 1035 | 24 | 0 | 757 | 24 | 23 | 4571 | 14 | 64 | 108 | 4 | 2 | 0 |
| 4.60 | 879 | 6017 | 4894 | 1064 | 59 | 1 | 154 | 59 | 162 | 3779 | 74 | 265 | 140 | 2 | 17 | 3 |
| 5.20 | 908 | 5863 | 4858 | 934 | 71 | 1 | 70 | 71 | 198 | 3758 | 81 | 263 | 113 | 17 | 2 | 3 |
| 5.48 | 933 | 5830 | 4862 | 887 | 81 | 1 | 41 | 81 | 230 | 3831 | 81 | 246 | 84 | 16 | 0 | 3 |
| 4.56 | 827 | 6688 | 5469 | 1199 | 20 | 0 | 915 | 20 | 26 | 5037 | 17 | 69 | 115 | 4 | 3 | 0 |
| 5.25 | 875 | 6500 | 5414 | 1031 | 55 | 1 | 238 | 55 | 193 | 4141 | 81 | 307 | 152 | 19 | 4 | 3 |
| 5.25 | 912 | 6582 | 5471 | 1042 | 69 | 1 | 92 | 69 | 255 | 4177 | 97 | 305 | 115 | 24 | 2 | 6 |
| 5.25 | 940 | 6611 | 5487 | 1045 | 79 | 1 | 52 | 79 | 301 | 4180 | 94 | 297 | 105 | 23 | 1 | 9 |
| 4.87 | 822 | 4807 | 3965 | 814 | 28 | 0 | 598 | 28 | 28 | 3551 | 16 | 64 | 86 | 4 | 2 | 13 |
| 5.23 | 877 | 4762 | 3944 | 754 | 64 | 1 | 119 | 64 | 162 | 3083 | 64 | 206 | 90 | 12 | 1 | 1 |
| 4.87 | 899 | 4791 | 3917 | 804 | 70 | 0 | 69 | 70 | 179 | 3027 | 69 | 208 | 81 | 14 | 2 | 4 |
| 5.18 | 931 | 4824 | 3967 | 766 | 91 | 1 | 40 | 91 | 240 | 3086 | 71 | 196 | 60 | 13 | 1 | 4 |
| 5.00 | 828 | 5276 | 4375 | 875 | 26 | 0 | 684 | 26 | 31 | 3978 | 16 | 72 | 97 | 3 | 1 | 0 |
| 5.15 | 872 | 5212 | 4324 | 840 | 48 | 1 | 160 | 48 | 142 | 3383 | 66 | 223 | 111 | 13 | 6 | 2 |
| 5.47 | 906 | 5234 | 4368 | 799 | 67 | 1 | 88 | 67 | 213 | 3370 | 75 | 232 | 86 | 15 | 3 | 5 |
| 5.42 | 932 | 5278 | 4399 | 812 | 67 | 0 | 45 | 67 | 218 | 3380 | 74 | 230 | 72 | 19 | 6 | 12 |

**Table 2.** Phenomenological models of OCM

| Model 1 | Model 2 | Model 3 | Model 4 |
|---|---|---|---|
| $r_1 = k_1 P^2_{CH_4} P_{O_2}$ | $r_1 = P_{CH_4} P_{O_2}$ | $r_1 = k_1 P_{CH_4} P_{O_2}$ | $r_1 = P_{CH_4} P_{O_2}$ |
| $r_2 = k_2 P_{C_2H_6} P_{O_2}$ | $r_2 = k_2 P_{C_2H_6} P_{O_2}$ | $r_2 = k_2 P_{C_2H_6} P_{O_2}$ | $r_2 = k_2 P_{C_2H_6} P_{O_2}$ |
| $r_3 = k_3 P_{C_2H_4} P_{O_2}$ | $r_3 = k_3 P_{C_2H_4} P_{O_2}$ | $r_3 = k_3 P_{C_2H_4} P_{O_2}$ | $r_3 = k_3 P_{C_2H_4} P_{O_2}$ |
| $r_4 = k_4 P_{CH_4} P_{O_2}$ | $r_4 = k_4 P_{CH_4} P_{O_2}$ | $r_4 = k_4 P_{CH_4} P_{O_2}$ | $r_4 = k_4 P_{CH_4} P_{O_2}$ |
| $r_5 = k_5 P_{CO_2} P_{H_2} - k_5 P_{CO} P_{H_2O}/K_p$ | $r_5 = k_5 P_{CO_2} P_{H_2} - k_5 P_{CO} P_{H_2O}/K_p$ | $r_5 = k_5 P_{CO_2} P_{H_2} - k_5 P_{CO} P_{H_2O}/K_p$ | $r_5 = k_5 P_{CO_2} P_{H_2} - k_5 P_{CO} P_{H_2O}/K_p$ |
| $r_6 = k_6 P_{C_2H_4} P_{O_2}$ | $r_6 = k_6 P_{CH_4} P_{O_2}$ | $r_6 = k_6 P_{CH_4} P_{O_2}$ | $r_6 = k_6 P_{C_2H_4} P_{O_2}$ |
| $r_7 = k_7 P_{CH_4} P_{O_2}$ | | $r_7 = k_7 P_{C_2H_6}$ | $r_7 = k_7 P_{C_2H_6}$ |
| $r_8 = k_8 P^n_{CH_4} P^m_{O_2}$, | | $r_8 = k_8 P_{C_2H_4} P_{H_2O}$ | $r_8 = k_8 P_{C_2H_4} P_{H_2O}$ |
| where $n = 1.86$, $m = 0.723$ | | $r_9 = k_9 P_{CO} P_{O_2}$ | |

**Table 3.** Kinetic parameters of models 1–4*

| Constant | Model 1 | | Model 2 | | ÌModel 3 | | Model 4 | |
|---|---|---|---|---|---|---|---|---|
| | $A_i$ | $E_i/R$ | $A_i$ | $E_i/R$ | $A_i$ | $E_i/R$ | $A_i$ | $E_i/R$ |
| $k_1$ | 21.16 | −13820 | 35.04 | −27820 | 34.54 | −27261 | 35.09 | −28585 |
| $k_2$ | 10.07 | −9910 | 40.47 | −30000 | 40.45 | −30000 | 39.76 | −30000 |
| $k_3$ | 33.32 | −23790 | 34.62 | −24758 | 29.68 | −18919 | 33.91 | −24065 |
| $k_4$ | 29.88 | −30000 | 37.03 | −32564 | 21.00 | −16729 | 29.94 | −30000 |
| $k_5$ | 9.83 | −3000 | 11.94 | −2000 | 12.71 | −8251 | 13.05 | −7950 |
| $k_6$ | 26.96 | −17380 | 17.07 | −16050 | 35.96 | −33942 | 26.78 | −16800 |
| $k_7$ | 36.55 | −30000 | – | – | 14.09 | −9931 | 28.06 | −21967 |
| $k_8$ | 16.62 | −30000 | – | – | 14.66 | −6460 | 29.60 | −25257 |
| $k_9$ | – | – | – | – | 16.35 | −3575 | – | – |

* $\ln k_i = A_i + E_i/RT$.

Discrimination of systems of stoichiometric chemical equations was carried by simulating the kinetic experiment reported in an earlier work [9] (Table 1). Because a correct kinetic description of complex reactions is possible only for particular compounds, we used the corresponding phenomenological models. In addition to the existing kinetic model developed earlier in order to approximate reaction system (I) [9], phenomenological models for approximating reaction systems (II)–(IV) were also constructed. For this purpose, using the least-squares method and the Davidon–Fletcher–Powell minimization method [38], we found the kinetic parameters providing the best fit to the experimental data presented in Table 1 and set up rate equations for the systems of stoichiometric equations (II)–(IV) (Table 2).

In model 1, the rate of methane oxidation into ethane is second-order with respect to methane and the rate of the $C_{3+}$ hydrocarbon formation reaction is of fractional order with respect to methane and oxygen (Table 2). In models 2–4, all rate equations are first-order with respect to the reactants. The calculated Arrhenius parameters of the reactions are listed in Table 3. We suppose that the rates have dimensions of

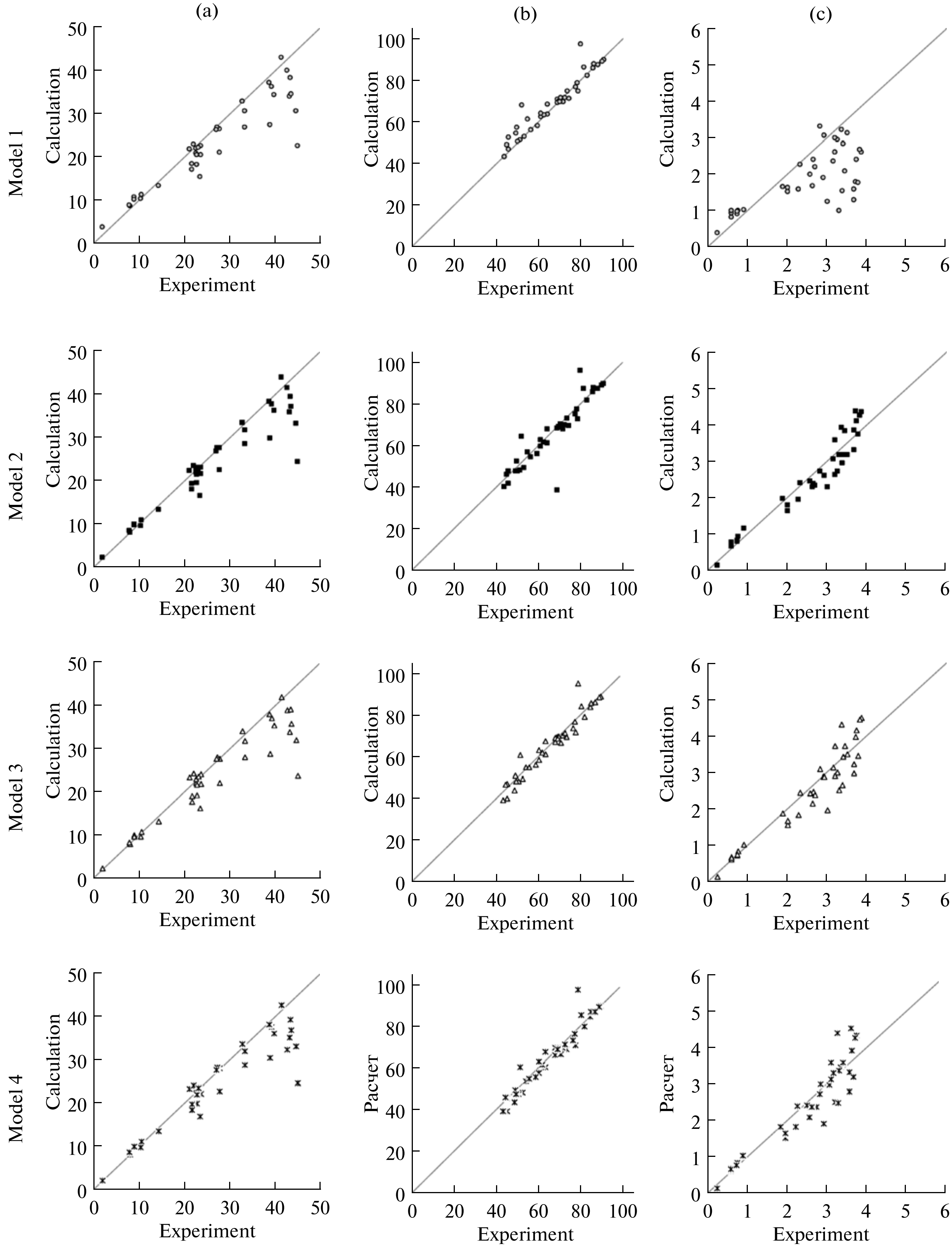


**Fig. 1.** Correlation plots for the (a) methane conversion, (b) $C_2$ hydrocarbon selectivity, and (c) ethylene : ethane ratio.

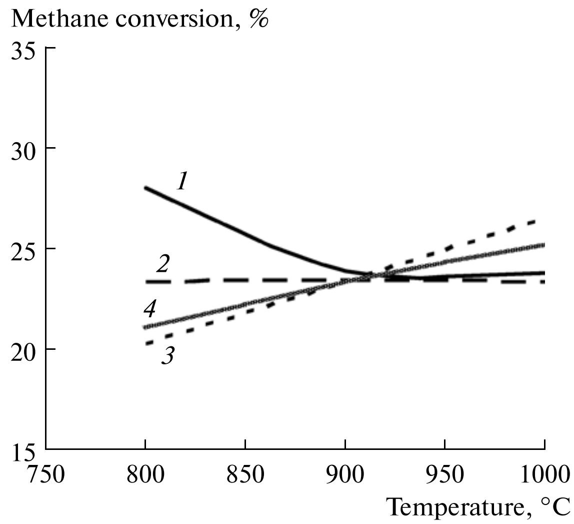


**Fig. 2.** Temperature dependence of the methane conversion ($P = 0.1$ MPa, oxygen conversion of 95%, $CH_4 : O_2 = 5$) calculated for models (*1*) 1, (*2*) 2, (*3*) 3, and (*4*) 4.

ml/h/g(Cat) and the partial pressures have dimensions of atm.

Using these kinetic parameters, we calculated the methane conversion, the $C_2$ hydrocarbon selectivities, and the ethylene : ethane ratio for the conditions of particular experiments. The results of these calculations are represented as correlation plots in Fig. 1.

It is clear from these plots that all of the four models provide a good fit, with a very small scatter of data points, to the experimental $C_2$ hydrocarbon selectivities. The experimental ethylene : ethane data are described well, also with a small scatter of data points, by models 2–4, while model 1 leads to a marked underestimation of these data. None of the models provides a good fit to the methane conversion data, with data points scattered in nearly the same way for all of the models.

It was, therefore, of interest to simulate the OCM kinetics in order to establish relationships between the methane conversion and basic process parameters. The simulation was carried out in the isothermal quasi-homogeneous plug flow reactor approximation for the conditions that were demonstrated in an earlier work [9] to be of greatest interest to the industry: excess methane ($CH_4 : O_2 = 5$), $P = 0.1$ MPa, and $T = 800–1000$°C (Fig. 2).

In model 1, raising the reaction temperature leads to a decrease in the methane conversion (Fig. 2). In model 2, the methane conversion is temperature-independent. In models 3 and 4, the methane conversion increase with an increasing temperature, and this is in agreement with experimental observations [28, 34].

The mean relative errors for the reactant concentrations calculated in the framework of the four models are given in Table 4.

It can be seen from Table 4 that, as compared to the other models, model 1 leads to the greatest errors for most reactants (16.4–21.4%) and model 4 leads to the smallest errors (13.2–17.0%). Therefore, model 4 is the most adequate.

Thus, we have examined different systems of stoichiometric equations approximating the OCM process over the Li–Mn–W/$SiO_2$ oxide catalyst. For these systems, we have developed phenomenological kinetic models describing the rates of variation of reactant concentrations and have determined the kinetic parameters. The OCM process has been simulated for an isothermal plug-flow reactor. Based on the results of this simulation, we have discriminated between possible OCM routes. The system of stoichiometric equations (IV) provides the best fit to the observed OCM kinetics.

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**Table 4.** Mean relative errors in the calculation of compound concentrations for models 1–4

| Compound | Relative error, % | | | |
|---|---|---|---|---|
| | model 1 | model 2 | model 3 | model 4 |
| $CH_4$ | 16.4 | 13.5 | 14.7 | 13.2 |
| $O_2$ | 19.2 | 16.8 | 16.5 | 15.7 |
| $C_2H_4$ | 24.2 | 14.5 | 15.9 | 17.0 |
| $C_2H_6$ | 19.0 | 13.2 | 12.2 | 10.2 |
| $CO_2$ | 20.4 | 29.1 | 20.8 | 15.6 |
| CO | 21.4 | 15.1 | 21.3 | 15.7 |

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