The Order of Product Formation in the Partial Oxidation of Methane to Syngas

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Abstract—The partial oxidation of methane to syngas is studied in the presence of Pt- and Ni-containing catalysts. The process kinetics does not provide unequivocal information on the order of formation of products (including carbon oxides) when either methane–oxygen or methane–oxygen–CO₂ mixtures are used. Experiments with ¹³C-labeled carbon dioxide added show the difference in the behavior of the catalysts. In the presence of Pt/ZrO₂, there is no noticeable transfer of the isotopic label to the CO molecules. On the nickel catalyst, ¹³CO is formed in substantial amounts, which can probably be explained by the redox reaction of ¹³CO₂ with metallic nickel under oxygen-free conditions behind the zone of the main reaction of methane oxidation.

INTRODUCTION

Reliable information on the order of product formation in the conversion of methane to syngas (CO + H_2) is important for a search for new catalytic systems and improving available systems and for optimizing the process as a whole. From this standpoint, an important question is whether carbon monoxide is the primary gaseous product of oxidation (as considered for the mechanism discussed in [1, 2]) or whether the main pathway to its formation is the macrosteps of steam or carbon dioxide reforming of methane, which follow the primary oxidation of methane to carbon dioxide and water (as proposed, for example, in [3–5]).

The goal of this study is to elucidate the order of product formation in methane oxidation. Specifically, we address the question of whether additional CO_2 introduced to the reaction mixture is involved in the formation of CO, and if it is, then at what stage and under which conditions. To answer these questions, we used the method of isotopic labeling (¹³C) of carbon dioxide.

EXPERIMENTAL

The processes of partial oxidation and carbon dioxide reforming of methane to form syngas was studied on the following catalysts: (1) the highly active supported Pt/ZrO₂ catalyst analogous to that described in [5] and (2) metallic foam nickel.

To solve the problem, we used the following methods:

(1) Comparison of the kinetic features of partial oxidation and carbon dioxide reforming of methane to syngas when they occur in separate (i.e., in the methane–oxygen and methane– CO_2 mixtures) and coupled (in the preliminary prepared methane–oxygen– CO_2 mixture) regimes and (2) The use of CO_2 labeled with the ¹³C isotope and the observation of the label transfer into CO.

In the experiments of the first type, we used a setup with a flow-type quartz reactor (i.d., 3.5 mm) and chromatographic analysis of products described in detail earlier [6]. A specific feature of the reactor unit is the presence of a reach-through hole normal to the axis in the central hottest part of the furnace. The reactor was mounted in this hole so that the catalyst layer is near the longitudinal axis of the furnace. In the absence of the reaction in this part of the reactor inside the furnace (~10 mm), the constant temperature is maintained (with an accuracy of $\pm 2^{\circ}$ C at working temperatures of up to 900°C). Outside of this hot zone, the temperature drastically decreases (the gradient is several hundreds of degrees for a furnace wall thickness of 2-3 mm). The uniformity of the temperature field in the hot zone and the drastic decrease in the temperature outside the furnace allow for the highly reliable control of the reaction space where methane conversion may occur, including homogeneous reactions and reactions initiated by the reactor wall surface or any other surfaces inside the reactor. Moreover, the above configuration of the reactor unit makes it possible to observe the temperature field inside the catalyst layer and outside of it through the open butt-ends and the transparent wall of the quartz reactor without inserting any measuring elements that could change the conditions of heat and mass transfer and affect the chemistry and kinetics of the reactions. Moreover, the mobile fastening of the furnace makes it possible to remove heating of the catalyst zone of the reactor for the shortest time and to replace the furnace with a socket which is not an active heater but which decreases heat loss by the reaction zone in the autothermal reaction due to its proper exothermicity without external heating.

W*, ml/min	P(excess), atm	[H ₂], vol %	[CH ₄], vol %	[CO ₂], vol %	[CO], vol %
100	0.30	8.30	36.24	33.94	21.14
200	0.70	5.90	40.07	38.43	14.49
95	5.75	6.00	39.64	39.19	13.70
200	5.75	3.30	44.48	43.33	8.280

Table 1. Composition of the reaction mixture in carbon dioxide reforming of methane

Note: Foam Ni, 300 mg; 49.5% CH_4 -49.5% CO_2 --1% Ni₂; 800°C. * *W* is the feed flow rate at atmospheric pressure.

Table 2. Changes in the composition of the reaction gas when the initial mixture (1) 65% CH_4 -35% O_2 is replaced by (2) 60% CH_4 -35% O_2 -5% CO_2

No. mix- ture	[CO], vol %	[CH ₄], vol %	[CO ₂], vol %	[H ₂], vol %
1	26.40	23.90	9.55	40.10
2	30.30	29.55	11.40	38.80

Note: Foam Ni, 300 mg; 200 ml/min flow; the frontal temperature is 520–535°C.

In this work we paid special attention to the appearance of autothermal regimes, the determination of the boundaries of their stability, and the regularities of product formation under these conditions. Therefore, we did not use any feedback to maintain a constant temperature in the reactor. In the case of external heating, its regime is set by applying a constant voltage to the coils of the furnaces; that is, the supplied electric power was controlled. The appearance of the very nonuniform temperature profile due to the highly exothermic oxidation of methane was observed by a change in the position of the thermocouple in the reactor and (especially in the runs when the thermocouple was not inserted into the reactor) by sight.

The reactor unit was identical to that used in the isotopic labeling experiments. The only difference in this case was the online mass spectrometric analysis of the mixture described in detail in [7].

Preliminarily mixed gaseous mixtures were used that contained methane, oxygen, and CO_2 . In the experiments with labeled CO_2 , the fraction of ¹³C was 84%.

RESULTS AND DISCUSSION

1. General Features of CO₂ Reforming of Methane and Methane Partial Oxidation in Separate and Combined Regimes

Nickel catalyst. On foam nickel, the efficient formation of syngas components was observed in methane– CO_2 mixtures at temperatures >800°C and flow rates of the feed gas <5 ml s⁻¹ g⁻¹ (see Table 1). The catalyst activity increased with time, and upon the completion of the process, the sample changed its color from faded gray to white and acquired a typical shine, pointing to the reduced surface and the absence of coke. With an increase in the flow rate, a decrease in the yield of CO and especially hydrogen was observed. An increase in the pressure led to a decrease in the yields of CO and hydrogen (in complete agreement with Le Chatelier's thermodynamic principle), while the above nature of the product composition was preserved.

In oxygen-containing mixtures, a noticeable dependence of the product composition on the feed rate was observed: an increase in the flow rate led to an increase in the concentration of CO and hydrogen and to a decrease in the concentration of CO_2 in the reaction mixture.

An increase in the heat load by an increase in the feed flow rate to 120–200 ml/min or 6.5-11 ml s⁻¹ g⁻¹ at a constant electric power of the furnace results in a change in the process regime: a hot zone is formed in the depth of the catalyst bed, which starts to move toward the gas flow. Simultaneously, the temperature of this zone increases. This transition regime lasts several seconds. As a result, the hot zone moves to the front layer of the catalyst bed and then the process becomes stationary and autothermal. That is, at a constant flow rate, it can occur when the voltage applied to the furnace is shut off or drastically decreased depending on the rate of the gas mixture supply.

At all rates of flow in the studied range, the apparent conversion of oxygen is at least 92–95% in the auto-thermal regime.

The experimentally observed nature of the dependence of the product yield on the flow rate points to the primary formation of CO and hydrogen, because the selectivity to these products increases with a decrease in the contact time (that is, with an increase in the flow rate). However, because CO_2 reforming of methane can occur on the same catalyst, such a dependence does not shed light on the ratio between two possible pathways of, for instance, CO formation: direct (from methane and oxygen) and consecutive (via the primary complete oxidation of methane to CO_2 and water and further carbon dioxide and steam reforming).

To obtain further information on the reaction pathways, we carried out experiments with the replacement of the methane–oxygen mixture with the triple methane–oxygen–CO₂ mixture. In these experiments the concentration of oxygen in the mixture was maintained constant (35 vol %), and some portion of methane (5 vol %) was replaced by CO₂ after the beginning of the autothermal regime at a flow rate of 200 ml/min. The results obtained are summarized in Table 2.

As the above data show, the addition of CO_2 to the initial mixture results in an increase in the CO concentration in the dry product gas and some decrease in the hydrogen concentration. In other words, the addition of CO_2 to the reaction mixture undoubtedly affects the process, but it is impossible to draw an unequivocal

conclusion about the formation of CO and hydrogen via carbon dioxide reforming of methane. An alternative explanation for the effect of CO_2 addition may be a shift in the equilibrium in the reaction of carbon dioxide reforming of methane and an indirect (via this equilibrium) effect on the position of the equilibrium in the water-gas shift reaction and in the steam reforming of methane. More definite conclusions can be drawn based on the experiments with ¹³C-labeled CO₂ (see below).

A very important question is the localization of the hot zone. If we place a small amount of quartz wool before the front layer of the catalyst, then it has a higher pyrometric temperature than the catalyst (even in its front layer) under the conditions of the settled autothermal process. The readings of the thermocouple whose thermojunction is deepened to ~ 1 mm in the front layer of the catalyst are noticeably lower than the pyrometric temperature of the hot zone (520-535 and ~750-800°C, respectively). When the thermocouple is pulled out of the catalyst bed, its readings start to depend on the flow rate in a complex manner: an increase in the load leads to an increase in the temperature measured by the thermocouple to a certain limit (due to the intensification of heat evolution); then, the cooling of the thermojunction with unreacted gases starts to dominate and leads to readings that are too low. The pyrometric temperature continues to increase with an increase in the load.

Pt/ZrO₂ catalyst. At relatively low flow rates of the mixtures 65% CH₄–35% O₂ and 60% CH₄–35% O₂– 5% CO₂, methane reforming on the Pt/ZrO₂ catalyst only occurs in the case of external heating; the main products of the reaction are CO₂ and water, and CO and hydrogen are formed in small amounts (usually, H₂ \geq CO).

If the mixture supply is sufficient for compensating the heat loss (that is, if the flow rates of the methane– oxygen mixture are rather high (>100 ml/min)), the "light-off" of the reaction with fast self-heating occurs at nearly room temperature. The regime of such a self-sustaining process is determined by the ratios of the residence times of the reaction mixture in different zones.

The most interesting case is when the amount of the catalyst is small (the formal contact time is <0.01 s). In this case, the following picture is observed for the settled regime: at a relatively low temperature of the catalyst ($\leq 600^{\circ}$ C), the space upstream the catalyst bed is strongly heated along the mixture flow due to the exothermic process of methane oxidation (to 800–900°C). Almost all the oxygen of the initial mixture is consumed by the reaction before reaching the catalyst bed for a period of ~0.01 s.

If a chromel–alumel thermocouple is placed in a quartz jacket downstream the Pt/ZrO_2 catalyst at different distances, then its readings correspond to the temperature profile along the reactor axis. In the typical settled process, the temperature right behind the active catalyst bed is ~580°C. Additional thermal insulation of the reactor with an asbestos socket leads to an increase

in the measured temperature to \sim 780°C. When the thermocouple is used without a jacket, its readings increase to \sim 1060°C in the absence of additional insulation and to 1070°C in the presence of additional insulation. However, the pyrometric temperature of the thermojunction is several hundred degrees lower. The reasons for such a difference are not quite clear, but the exothermic process of free radical decay on the metallic surface of the thermocouple probably contributes most greatly to the observed phenomena. There is further evidence for the fact that heat transfer from the hot zone of methane oxidation does not determine thermocouple heating behind the catalyst bed:

(i) The independence of thermocouple readings at a distance of 5-10 mm downstream the catalyst bed on the additional thermal insulation of the reactor;

(ii) The observed coking of the thermocouple junction at a distance of 5 mm from the catalyst bed; a growth of the friable coke layer leads to a decrease in the temperature measured by the thermojunction (from ~450 to 125° C); at some points, the coke layer peels off and the measured temperature drastically increases to 320° C and then the whole cycle repeats.

The possibility of secondary reactions of radicals (formed in the catalytic activation of methane) on the material of the chromel–alumel thermocouple with a change in the apparent conversion and product composition was shown earlier (see, for instance, [6, 7]). In this work, we failed to detect a change in the composition of the gaseous products of the reaction when the jacket-free thermocouple was placed downstream the catalyst bed. Apparently, we can only assume additional anaerobic methane conversion because oxygen is almost completely absent from the gas phase. The extent of such conversion is too small to be detected against the background of the high methane conversion at earlier process stages.

The above experiments show that the process probably occurs in the following manner: the active catalyst generates active species (the products of incomplete oxidation or free radials, which is more likely); the latter diffuse to some distances to the gas phase toward the gas flow to the zone upstream the catalyst and initiate a homogeneous reaction there, where the mixture is still rich in oxygen. Nevertheless, the concentration of oxygen in the mixture is insufficient for purely homogeneous gas-phase combustion. Note that there are no steps in the homogeneous oxidation of methane where a CO₂ molecule is formed bypassing the primary formation of CO (see, for instance, [8, 9]). In other words, CO_2 cannot be the primary product because it is only formed via the reactions of CO with oxygen-containing species, mostly radicals:

$$CO + RO' \longrightarrow CO_2 + R'$$
 (I)

or

$$CO + RO_2 \longrightarrow CO_2 + RO',$$
 (II)



Fig. 1. Mass spectra of (*1*) the initial mixture 60% CH_{4} -35% O_2 -5% $^{13}CO_2$ and the reaction mixtures when (2) $^{13}CO_2$ and (3) $^{12}O_2$ are added in the autothermal regime on the Pt/ZrO₂ catalyst.

where R is an organic (e.g., hydrocarbon) radical or a hydrogen atom.

Interestingly, the process selectivity can be changed if a small amount of less active catalyst capable of complete methane oxidation to CO₂ (MgO) is placed upstream the Pt/ZrO_2 bed. The relative fraction of CO_2 in the reaction gases increases, but the selectivity does not change if the SiO₂ (silica gel) packing is used. These results provide a better understanding of the process in the presence of this Pt-containing catalyst. It is likely that, in the presence of the hot metallic surface, the homogeneous oxidation of methane in the gas phase is initiated before the catalyst. We should stress that the presence of the active catalyst is necessary for that, because the limiting reactant (oxygen) cannot be converted in full in the mixture with this composition under conditions of a purely gas-phase process at the same temperatures. The product composition is determined by the process in the precatalytic zone: in complete agreement with the regularities of homogeneous oxidation, the main products are CO and hydrogen and the fraction of CO₂ increases when a material active in the complete oxidation (MgO in our case) is placed in the zone before the Pt-containing catalyst. When the arrangement of zones (material beds) is reversed, there is no effect from adding the second component.

Visual examination of the process of autothermal regime settling in the presence of foam nickel (see above) and the regularities of product formation led us to assume that the predominant gas-phase oxidation of methane in the precatalytic space also takes place in the case of this catalyst.



Fig. 2. Mass spectra of (*1*) the initial mixture 60% CH_{4^-} 35% O_2 -5% $^{13}CO_2$ and the reaction mixtures when (2) $^{13}CO_2$ and (3) $^{12}O_2$ are added in the autothermal regime on foam nickel.

2. Methane Conversion in the Mixture Containing ¹³CO₂

Experiments with the addition of ¹³C-labeled carbon dioxide to the initial methane-oxygen mixture were carried out to reveal the ratio between the routes of CO formation. In these experiments, after the autothermal regime is settled, the ionic current of the mass spectrometer was recorded for m/e ranging from 1 to 48 (Figs. 1, 2). In this range, masses corresponding to the fragments of the hydrogen, methane, and water molecules (m/e = 1), molecular hydrogen ion (m/e = 2), fragments of the methane (m/e = 12-16) and water molecules (m/e = 16-18), ¹²CO (m/e = 28), ¹³CO (m/e = 29), molecular oxygen ion (m/e = 32), ¹²CO₂ (m/e = 44), and ${}^{13}\text{CO}_2$ (m/e = 45) were registered. The peak at m/e = 16 is a complex combination of molecules of methane, water carbon oxides, oxygen, and doubly ionized molecular oxygen. The criterion for the formation of CO from CO_2 in our experiments is the appearance of ions with m/e = 29 in the mass spectrum. Note that the low-intensity signal of these ions is also registered when the initial mixture is analyzed; it is likely that the spectrum contains the signal of ¹³CO, which is a fragment of the ${}^{13}CO_2$ molecule and which is formed under the action of the electron impact in the ionization chamber of the mass spectrometer. Furthermore, even in the mixtures that do not contain ¹³C-labeled molecules, low-intensity signals with m/e = 29 and 45 and signals with m/e = 28 and 44 were observed for the room-temperature mixture that does not contain added CO₂. Apparently, all of them are the components of residual gases in the vacuum chamber. Tables 3 and 4 show the values of the peak intensities corresponding to the molecular ions of carbon oxides with different isotopic compositions registered under different conditions.

Conditions	m/e										
	1	2	15	18	28	29	32	44	45	(28/44)	(29/45)
Room temperature, ${}^{13}\text{CO}_2$	0.00318	0.00196	0.84448	0.07009	0.11150	0.00979	0.75111	0.00275	0.06331	40.55	0.00782
ATR*, ¹³ CO ₂	0.00704	0.01755	0.51893	0.52911	0.39557	0.01421	0.02719	0.23563	0.06007	1.22	0.106
ATR, $^{12}CO_2$	0.00813	0.03494	0.48036	0.52353	0.46072	0.00837	0.03114	0.29301	0.00509	1.20	1.645

Table 3. Intensities of mass spectrum signals corresponding to reactants and the main products in the oxidation of methane on the Pt/ZrO_2 catalyst

* ATR stands for the autothermal regime.

Table 4. Intensities of mass spectrum signals corresponding to reactants and the main products in the oxidation of methane on foam Ni

Conditions	m/e										
	1	2	15	18	28	29	32	44	45	(28/44)	(29/45)
Room temperature, ${}^{13}\text{CO}_2$	0.00318	0.00196	0.84448	0.07009	0.11150	0.00979	0.75111	0.00275	0.06331	40.55	0.00782
ATR*, ¹³ CO ₂	0.00455	0.10709	0.26829	0.22807	0.36673	0.04180	0.04011	0.26099	0.04941	0.988	0.741
ATR, ${}^{12}CO_2$	0.00399	0.10724	0.17977	0.23041	0.49042	0.00934	0.04265	0.39113	0.00561	0.976	1.664

* ATR stands for te autothermal regime.

Table 3 shows that, in the presence of the Pt/ZrO₂ catalyst, the replacement of the initial ¹²CO₂ mixture by ¹³CO₂ does not lead to a considerable change in the ratio of the intensities of peaks at m/e = 28 and 44, which should have taken place in the case of the substantial contribution of the consecutive route of CO formation via the intermediate complete oxidation of methane to CO₂ according to the reaction

$${}^{12}\text{CH}_4 + {}^{13}\text{CO}_2 \longrightarrow {}^{12}\text{CO} + {}^{13}\text{CO} + 2\text{H}_2.$$
 (III)

This conclusion is supported by the analysis of the ratio of peak intensities at m/e = 28, 29, 44, and 45 in the mass spectra registered with an increase from room temperature to ~950 K: at a certain decrease (~5%) in the intensity of the peak at m/e = 45 and the corresponding increase in the intensity of the peak at m/e = 29 compared to the background values, the ratio of intensities calculated taking into account the background values (shown in boldface in Table 3) differs greatly from the peak intensity ratio for the molecular ions ¹²CO and ¹²CO₂. This also shows the preferred formation of CO molecules via the direct pathway immediately from methane and without the complete oxidation of methane to CO₂.

Comparison of data shown in Tables 3 and 4 shows a substantial difference in the behavior of the isotopic label added with the CO₂ molecule in the case of the reaction on Pt/ZrO₂ and foam nickel. The ratio of signal intensities at m/e = 28 and 44 in the case of the reaction on the foam nickel is almost independent of the isotopic composition of CO₂ added to the reaction. This would be hard to explain if the contribution of reaction (III) were considerable. It is close to that observed in the reaction on the Pt/ZrO catalyst (~0.98 and ~1.21, respectively), whereas the ratio of the concentrations of carbon oxides containing ¹³C changes by a factor of 7 when Pt/ZrO₂ is replaced by foam nickel. It can be easily shown that, at the same conversions of carbon dioxide in the reaction with methane, the ratio of concentrations of ¹³CO₂ and ¹³CO in the case of reaction (III) should be half that of ¹²CO₂ and ¹²CO in the reaction

$$CH_4 + {}^{12}CO_2 \longrightarrow 2{}^{12}CO + 2H_2.$$
 (IV)

Indeed, if carbon monoxide were only formed via the consecutive mechanism, the expected ratio of signal intensities in the carbon dioxide reforming of methane could be estimated on the basis of the following assumptions. Let us denote the yields of ¹³CO from ¹³CO₂, ¹²CO from ¹³CO₂, and ¹²CO from ¹²CO₂ by $Y_{13/13}$, $Y_{12/13}$, $Y_{12/12}$, respectively. Under the same conditions, we can write for reactions (III) and (IV)

$$Y_{12/12} = Y_{12/13} + Y_{13/13}.$$

$$Y_{13/13} = Y_{12/13},$$

we conclude that

Because

or

$$Y_{13/13} = 0.5Y_{12/13}$$

$$J(28)/J(44) = 2J(29)/J(45)$$

where J(m/e) are the intensities of the peaks corresponding to a given m/e value in the mass spectrum.

However, radically different relationships are observed in the experiment, and they cannot be explained by the occurrence of carbon dioxide reforming of methane:

- in the presence of the Pt/ZrO₂ catalyst:

– in the presence of foam nickel:

$$J(28)/J(44) \approx 1.37J(29)/J(45).$$

The relationships observed can be explained by the absence of any considerable involvement of carbon dioxide in the reaction with methane in the presence of oxygen. As concerns foam nickel, the experimentally determined difference in the ratios of signal intensities at m/e = 29 and 45 and m/e = 28 and 44 is much smaller than possible in the case of reactions (III) and (IV) (only ~30%). If we also take into account the possibility of steam reforming of ${}^{12}CH_4$ molecules, this difference should be even greater. This led us to assume the presence of the pathway of carbon dioxide conversion into carbon monoxide via the reaction that is not connected to methane conversion. It is most likely that the interaction of CO₂ with reduced nickel is such a pathway:

$$Ni + CO_2 \longrightarrow NiO + CO.$$
 (V)

This reaction can be coupled with the reduction of NiO by any reducing agent available in the reaction mixture:

$$NiO + CH_4 \longrightarrow Ni + (H_2, H_2O, CO, CO_2),$$
 (VI)

$$NiO + CO \longrightarrow Ni + CO_2,$$
 (VII)

$$NiO + H_2 \longrightarrow Ni + H_2O.$$
 (VIII)

It can be easily shown that only the combination of reactions (V) and (VI) can be considered as carbon dioxide reforming of methane, whereas the combination of reactions (V) and (VIII) and the reverse gives us the water-gas shift equilibrium (which is also accompanied by the transfer of the label and an increase in the ratio $[{}^{13}CO_{2}]$).

The key factor that determined the difference in the behavior of the two catalysts under consideration may be the different capabilities of the active metals to be oxidized by carbon dioxide. In the case of nickel, this process is quite possible (the calculation of the heat effect according the data from [10] gives us the value $\Delta H = 38.5$ kJ/mol), which allows the occurrence of steps (V) and (VII) in the framework of the single redox process resulting in the formation of isotopically labeled carbon monoxide in considerable amounts. At the same time, a reaction analogous to (V) for platinum is much less probable ($\Delta H \approx 210$ kJ/mol), and the carbon dioxide reforming on Pt-containing catalysts can probably occur only under strictly anaerobic conditions via a mechanism other than steps (V) and (VI).

Such a mechanism can be, for instance, the interaction of CO_2 with the products of dissociative chemisorption of methane on reduced metal. Thus, Bychkov et al. [11] concluded, based on their study of the process of methane and CO₂ interaction with Ni-containing catalysts, that the main pathway of CO formation in carbon dioxide reforming of methane on these systems is the interaction of CO_2 with the products of methane dissociation on the reduced nickel surface. Hydrogen is formed in the dissociative chemisorption of methane, which also requires a reduced metallic surface. If one could show that residual oxygen, which is almost always present in the reaction mixture of oxy reforming and combined reforming, does not prevent the occurrence of this process at a high rate, there would be strong evidence for the involvement of CO_2 in this reaction with methane. Note, however, that the experiments were carried out in this work in strictly anaerobic conditions. This fact makes it difficult to use these results in analyzing the processes occurring in triple (i.e., oxygen-containing) initial mixtures. Nevertheless, the results reported in [11] support the possibility of the above redox process on Ni-containing catalysts.

CONCLUSION

The results of this work show that the main pathway for the formation of products of partial methane oxidation (carbon monoxide and hydrogen) in the presence of Pt-containing catalysts is the direct one, which is the oxidation of methane with oxygen. Carbon dioxide added to the reaction mixture is not involved in the reaction at short contact times. On a foam nickel catalyst, CO₂ added to the reaction mixture partially converts to oxidize reduced metal; however, in this case, the direct pathway of CO formation from methane by oxidation with oxygen also exists.

Special attention should be given to the process occurring in the autothermal regime. Unfortunately, at this stage it is hard to be certain regarding the mechanism of its formation, its dynamics, and spatial localization of steps. However, we can state that macrokinetic factors play an important role here with a high degree of probability. Two limiting cases are considered in the literature:

(i) Light-off of the active catalyst surface due to the exothermic effect of the catalytic reaction [12]; in this case, the noncatalytic reaction in the gas phase does not occur;

(ii) light-off of the gaseous mixture heated by the surface [13], which is considered as a hot but chemically inert wall.

The case considered in this work differs in that the surface probably affects the process not only (or not mainly) thermally, but it intensively generates active species, including free radicals, and initiates the chemical gas-phase reaction. Undoubtedly, secondary reactions of chain carriers can occur on the same surface, and this fact complicates the picture even more. It is difficult to say to what degree the light-off of the gaseous mixture in the zone upstream the catalyst is determined by heating from the hot catalyst surface and to what degree this is due to the additional initiation of active species escaping from the surface and diffusing toward the flow. To answer all the related questions, additional experiments with pyrometric measurements of the temperature profile along the reactor axis (in the catalyst bed and outside in both directions) are needed. Modeling is also needed that would take into account both heterogeneous and homogeneous reactions of all species which are present in the gas phase in methane oxidation and the processes of mass and heat transfer. Although there are recent papers in which the modeling of complex heterogeneous-homogeneous processes is approached (see, for instance, [14-20]), this task remains rather complex and has no general solution for schemes that differ in chemical and macrokinetic systems "gas-phase reaction-solid catalyst."

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