Direct Catalytic Oxidation of Methane to Formaldehyde: New Investigation Opportunities Provided by an Improved Flow Circulation Method

I. I. Bobrova, N. N. Bobrov, L. G. Simonova, and V. N. Parmon

Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia
E-mail: bobrova@catalysis.nsk.su
Received December 14, 2005; in final form, June 27, 2006

Abstract—An improved flow circulation reactor with reaction mixture quenching was used to study the direct oxidation of methane to formaldehyde at 600–770°C, a CH_4/O_2 volume ratio of 1 : 1 in the starting mixture, and gas mixture flow rates of 0.4–2.0 l/h. It was found that, in the presence of a surface containing SiO_2 (quartz reactor walls, the surface of silica packing materials, or the surface of SiO_2 as a catalyst constituent), the process occurred by a heterogeneous–homogeneous mechanism with chain continuation in the volume of a gas phase. The process was controlled by the size and shape of the free reaction volume, the contact surface area, and the residence time of a mixture in the reaction volume. The introduction of typical oxidation catalysts containing, for example, Pt or V_2O_5 as an active component along with SiO_2 resulted in a decrease in the yield of and selectivity for formaldehyde.

INTRODUCTION

The traditional industrial technology for the manufacture of formaldehyde is multistage: initially, synthesis gas is produced from natural gas (methane); then, methanol is produced from the synthesis gas; and, finally, formaldehyde is produced by the oxidative dehydrogenation of methanol. The single-stage manufacture of formaldehyde by the direct partial oxidation of methane with molecular oxygen, for example, in the presence of heterogeneous catalysts would be much more attractive. Studies in this area have been performed since the end of the 19th century; however, the resulting performance characteristics of the process, the yield of and selectivity for formaldehyde, are of no practical interest [1–3].

The direct selective oxidation of methane to formaldehyde at sufficiently high temperatures (>600°C) has not met with success mainly because formaldehyde is more reactive than methane under these conditions; therefore, it is readily further oxidized to carbon oxides [4]. On the majority of catalysts tested in the selective oxidation of methane under conditions of a flow reactor, the yield of formaldehyde (the amount of CH_4 (in mol %) converted into CH_2O in a single run of the reaction mixture through the reactor) was even lower than 1% [1–3]. This parameter was 2–4% for catalytic systems recognized to be the most promising systems [1–3]. In the majority of cases, the selectivity of methane conversion into formaldehyde above 50% was observed only at very low (less than 2%) degrees of methane conversion. Only a few publications [5–8] reported higher

yields of formaldehyde (5–9%) obtained on particular catalysts under flow reactor conditions without the addition of any initiators; however, as a rule, these data have not been reproduced by other researchers [2, 3, 9].

Catalysts based on silicon dioxide have been recognized to be most selective among promising methane oxidation catalysts. The properties of these catalysts, in particular, V_2O_5/SiO_2 and MoO_3/SiO_2, have been studied in sufficient detail; however, the role of SiO_2 in the test process remains unclear. Arutyunov and Krylov [3] believed that, unlike, for example, Al_2O_3, SiO_2 is inactive in the reactions of free radicals and other intermediates formed in the oxidation of methane on V_2O_5 and MoO_3; as a result of this, the oxidation process stopped at formaldehyde. On the contrary, Spenser [10] and Parmaliana et al. [11] suggested that the active sites of partial methane oxidation occur on the surface of SiO_2, whereas V_2O_5 and MoO_3 only modify the catalytic properties of SiO_2, in particular, by facilitating activation of oxygen at the catalyst surface. The high activity and selectivity of pure silica samples have been demonstrated in well-known publications (e.g., [12–14]). Thus, Kastanas et al. [12] detected noticeable amounts of CH_2O in an empty reactor of glass containing 96% SiO_2 even at 620°C.

Sun et al. [14] assumed that reactive siloxane sites (strained siloxane bridges), which are generated on the surface of silica in the course of dehydroxylation at a high temperature (>600°C), can be the sites of CH_4 activation on SiO_2. Methane can be chemisorbed at these sites with the formation of intermediate surface

methoxy ($\equiv$Si–O–CH$_3$) and/or methyl ($\equiv$Si–CH$_3$) groups. The dissociation of these groups at a high temperature (700°C) affords formaldehyde CH$_2$O [15] and/or CH$_3^{\bullet}$ free radicals, respectively. The methyl free radicals released into a gas phase do not undergo adsorption once again on the surface of SiO$_2$ [14, 16]; however, they can form ethane in the gas phase. Arutyunov and Krylov [3] assumed other reaction paths for formaldehyde formation on SiO$_2$. Parmaliana et al. [17, 18] related the observed activity of silica to the occurrence of trace impurities like Fe^{3+} ions inserted into an oxide matrix in the course of preparation rather than strained siloxane bridges. In a number of cases, either the results of a comparison between the activities of individual SiO$_2$ and catalysts prepared on its basis were contradictory or the observed differences were insignificant [16]. Finally, in attempts to systematize a great body published data, it was noted that general regularities in searching catalysts are difficult to reveal and experimental results are ambiguous and poorly reproducible [1–3].

To explain the direct oxidation of methane to formaldehyde in the presence of heterogeneous catalysts, heterogeneous–homogeneous and purely heterogeneous reaction schemes were proposed [3]; actually, these are two qualitatively different approaches to process organization.

Even in the early 1960s, Stadnik and Gomonai [19, 20] reported on the effects of temperature, the nature of reactor material, and the surface state of the reactor walls on the yield of formaldehyde in the reaction of methane oxidation. They also found that the addition of water vapor to a reaction mixture increased the selectivity of the process for formaldehyde [19]. More recently, Margolis et al. [21] detected CH$_3$O$_2^{\bullet}$ radicals by freezing free radicals from a reaction mixture of methane oxidation on SiO$_2$ in a CO$_2$ matrix and Nersesyan et al. [22] found a correlation between the yield of CH$_2$O and the concentration of HO$_2^{\bullet}$ and CH$_3$O$_2^{\bullet}$ peroxide radicals, which were detected using EPR spectroscopy, in the reaction vessel volume. These and other process peculiarities, in particular, a change to a self-oscillating mode under certain conditions [23], unambiguously suggest a heterogeneous–homogeneous mechanism of methane oxidation to formaldehyde in the presence of heterogeneous catalysts.

In this context, it is of interest that Baldwin et al. [9] attempted to find real advantages in the use of catalysts for the partial oxidation of methane to formaldehyde because similar conversion and selectivity values can be obtained in an uncatalyzed reaction simply by increasing reactant pressures. It was found that the same yield of formaldehyde (3.5%) as that on the best oxide catalysts can be obtained in an empty quartz tube reactor at a pressure of 5 atm and 625°C. Thus, Baldwin et al. [9] noted that the possible contribution of homo-

geneous gas-phase reactions, which can exert a considerable effect on the rate of reaction and the distribution of products, should be taken into consideration in a study of the reaction in the presence of heterogeneous catalysts. In turn, the contribution of homogeneous gas-phase reactions depends on temperature, the composition of the reaction mixture, and the organization of the reaction volume [9, 16, 24]. In this case, Banares et al. [24] noted the ambiguous role of a catalyst in the heterogeneous–homogeneous process. On the one hand, a catalyst initiates the reactions of target product formation by generating radicals; on the other hand, the catalyst terminates useful reactions by adsorbing active radicals from a gas phase. Moreover, the catalyst accelerates the reactions of formaldehyde oxidation and decomposition. Baldwin et al. [9] believed that any catalyst that activates methane more readily activates (decomposes or oxidizes) formaldehyde. Thus, the yield of formaldehyde in a purely homogeneous gas-phase oxidation reaction [9] was found to be higher than that obtained under the same conditions but in the presence of Fe/W and Fe/Mo oxides. According to Baldwin et al. [9], none of the well-known catalysts with reproducible results of testing can provide noticeable advantages of catalytic methane oxidation over pure gas-phase oxidation, although the gas-phase oxidation of methane is highly sensitive to minor changes in process parameters and, consequently, is difficult to control and thus noncompetitive.

Only a few examples of the target-oriented use of methane oxidation under heterogeneous–homogeneous conditions are known. Among them is a study of Yu et al. [25], who used as a reactor a quartz tube with a quenching device arranged within it and Na$_2$B$_4$O$_7$ supported on the walls of the tube. In this reactor, a formaldehyde yield of 20.5% was obtained on the addition of NO and water vapor to a methane–oxygen mixture.

However, the majority of researchers, who accepted the possibility of a heterogeneous–homogeneous catalytic reaction of methane oxidation, believed that the occurrence of the reaction in a gas volume resulted in target product losses. Therefore, homogeneous radical reactions should be suppressed in studying the process.

The most common heterogeneous reaction schemes have been discussed previously [4, 10, 14, 18, 26–29]. These reaction schemes differ in the nature of the steps of methane and oxygen activation and formaldehyde formation. A predominant opinion is that the rate of reaction is limited by the reaction of methane with active sites on the catalyst surface to form adsorbed CH$_3^{\bullet}$ radicals, the subsequent transformations of which on the surface result in formaldehyde formation. According to published data [10, 18, 26–29], the average values of the apparent activation energy of heterogeneous formaldehyde formation are 140–230 kJ/mol. Under certain assumptions, the reaction schemes proposed [18, 26–29] adequately described experimental data, which were mainly obtained at 500–650°C. Evi-

dently, the rate equations proposed were restricted to chosen conditions, under which optimum yields and selectivities for formaldehyde cannot be reached.

The above and other ambiguities and contradictions in the concepts of the role of a heterogeneous catalyst in the direct oxidation of methane to formaldehyde and the mechanism of this process invite further investigation with the use of new approaches and more sophisticated experimental techniques.

As noted above, the main body of experimental data on the test process was obtained with the use of flow microreactors. As an example, we can cite publications [10, 28], which describe in sufficient detail a traditional testing procedure for selective methane oxidation catalysts. In accordance with the description given, the procedure in use can be characterized as an approximate integral flow method. Bobrov [30] considered in detail a typical implementation procedure and special features of this method. It is well known that the method is characterized by simple experimental design, high throughput, and versatility, which are responsible for its wide use. The main disadvantage of this method is the impossibility of providing identical conditions for testing various catalysts and, consequently, the dependence of the resulting experimental data on a large number of difficult-to-control factors related to both catalysts and test processes. This disadvantage increases many times in the case of selective methane oxidation when the reaction product formaldehyde much more readily reacts with oxygen than the starting reactant methane. As a consequence, the reliability of the resulting data on the process mechanism and the properties of catalysts is dramatically impaired because the properties of a catalyst under specified test conditions only indirectly affect the result of an integral process.

In this context, a commonly used characteristic of catalytic properties such as the space time yield (STY) of formaldehyde, which is defined by the rate of formaldehyde buildup (g/h) per catalyst unit weight (kg), seems inappropriate for an objective comparison of catalysts. Moreover, the above procedure for the evaluation of catalysts for methane oxidation to formaldehyde implies the purely heterogeneous occurrence of the test process. Special care is taken to perform a heterogeneous process; in particular, either reactors with a minimum free volume upstream and downstream of the catalyst bed are used or this volume is filled with an inert packing material [10, 28]. At the same time, it was found previously [31, 32] that free-radical reactions can also occur in voids between catalyst particles to affect significantly the kinetics of oxidative methane transformations. A decrease in the amount of a catalyst, the dilution of a catalyst with a quartz packing, and the arrangement of a packed quartz bed upstream of the catalyst bed (for heating the inlet gas mixture) generate favorable conditions for the development of radical reactions in a gas phase. In this context, note that the highest STY values (1300 and 2200 g (kg Cat)$^{-1}$ h^{-1} [18,

33]) were obtained with very small catalyst loadings (0.005–0.05 g) in circumstances where the probability of methane oxidation occurring by a heterogeneous–homogeneous mechanism was high and the contributions of a homogeneous component to the overall rate of reaction could be very large.

Catalysts can be compared much more objectively with the use of precise differential techniques for studying catalytic properties; these techniques allow one to generate ideal stirring conditions in a laboratory reactor [34]. Under these conditions, the catalyst bed is isothermal and the contact reaction mixture over the surface of all catalyst grains has practically the same composition. A considerable experience in the development and use of flow circulation reactors (FCRs) in which a stirring device (circulation pump) is arranged outside of the reaction volume was acquired at the Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences. In particular, Bobrov et al. [31, 35, 36], who used FCRs to study the kinetics of catalytic methane steam reforming, obtained previously unknown data that suggest a considerable heterogeneous–homogeneous component in the mechanism of this most important industrial catalytic process. Therefore, it was of considerable interest to apply this FCR method to studies of the reaction of methane oxidation to formaldehyde.

The first attempts to perform methane conversion into formaldehyde using a flow circulation procedure were made as early as the end of the 19th century [3]. However, this technique was developed only in the middle 20th century [20, 37, 38]; FCRs with external stirring devices, which were originally proposed and implemented in the Soviet Union [39], were first used to perform the above process. Bobrov and Parmon [34] described in detail the design of FCRs and the procedure used for determining catalytic activity, as well as the design of FCRs and flow circulation systems. The main advantages of these reactors are the following: a controllable flow of the reaction mixture through the catalyst bed, a gradientless catalyst bed that is constant to a high degree under changes in the feed rate of the starting reaction mixture to the reactor, and the reliable maintenance and control of an isothermal catalyst bed. The use of FCRs for the oxidation of methane to formaldehyde allows one to obtain high selectivity for formaldehyde at very low methane conversions during a run of the reaction mixture through the reactor. In the case of selective oxidation reactions, an unambiguous advantage of FCRs is the possibility of instantaneously removing unstable products from the reaction mixture after each its passage through the reactor (the use of a quenching device).

Gomonai [37] used FCRs with reaction mixture quenching to study hundreds of aluminosilicate and phosphate catalysts and reached the integrated yield of formaldehyde $Y = 18\%$ at the process selectivity for formaldehyde $S = 94\%$ on the best of these catalysts at

650°C for a CH_4–O_2 mixture (2 : 1) [40]. In the cited work, a quartz tube 30 mm in diameter and 290 mm in length served as the reactor; formaldehyde and water vapor were condensed in a condenser. The catalyst was supported on a porcelain packing material treated with potassium tetraborate. To suppress homogenous steps, the free volume over the catalyst was filled with the same packing material. Quartz and glass were also used as packing materials in the cited work. According to Gomonai [37], the measures taken were responsible for the heterogeneous occurrence of the process, although experiments that supported this assumption were not performed (for example, experiments with an empty reaction volume or with varied amounts and particle sizes of the catalyst loaded). The circulation ratio reached (the ratio of the circulation rate to the rate of the reaction mixture at the reactor outlet) was no higher than 70; this considerably restricted the capabilities of the method. According to patent data [40], the residence time (t_r) of the mixture in an empty reaction volume (50 cm^3) during a run of the mixture through the reactor at a maximum circulation rate of 160 l/h was about 1 s. The filling of the reaction volume with catalyst grains (2–3 mm) decreased the value of t_r to ~0.5 s.

Note that only Gomonai [37] proposed the use of FCRs with mixture quenching as a method for comparative tests of catalyst activities in the process of selective methane oxidation. Other researchers [38, 41] used an FCR system in order to improve the performance characteristics of the process and considered it primarily as a nontraditional procedure for the production of formaldehyde. Thus, Mukhlenov et al. [38] increased the integral yield of formaldehyde to 42% using a circulation batch reactor (circulation of a reaction mixture in a closed space) with the absorption of formaldehyde in an absorber with water. However, this result is of no industrial importance because the process proposed is a non-steady-state batch process.

Of foreign researchers, only Vayenas et al. [41] used in experiments a system in which a reactor, a formaldehyde absorber, and a circulation pump formed a flow circuit in accordance with a typical flow chart of FCRs with an external stirring device. The maximally reached circulation ratio of a mixture was no higher than 100. The reported [41] residence times of a mixture in the reactor t_r = 30–150 s were obtained by dividing the reactor volume (25 cm^3) by the feed rate of the initial reaction mixture (0.6–3.0 l/h) without considering the circulation of the mixture in the circuit. Actually, the value of t_r was equal to 1.5 s at a maximum circulation rate of the mixture equal to 60 l/h. Distilled water heated to 77°C was chosen as the best formaldehyde absorbent. Vayenas et al. [41] increased the integral yield of formaldehyde to 50% at S = 56% by oxidizing methane on a V_2O_5/SiO_2 catalyst at a low methane feed rate of 0.014 l/h and a catalyst temperature of 620°C. Note that this result was obtained in a 25-cm^3 quartz reactor, the major part of which remained empty upon loading the catalyst (1.9 g). This generated favorable
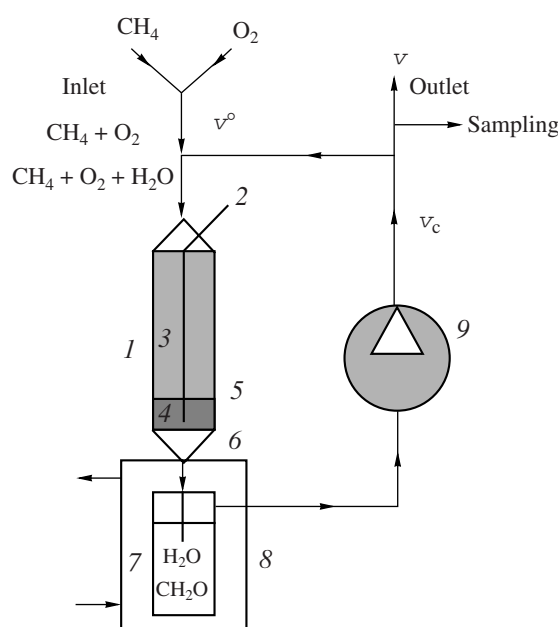

Fig. 1. Schematic diagram of a flow circulation reactor with reaction mixture quenching: (*1*) reactor, (*2*) thermocouple, (*3*) quartz-packed volume for heating the initial reaction mixture, (*4*) reaction volume, (*5*, *6*) quartz glass grates, (*7*) thermostat (20°C), (*8*) quenching device, and (*9*) circulation pump; v_c is the circulation flow rate of the reaction mixture, $v°$ is the feed rate of the initial reaction mixture, and v is the flow rate of the reaction mixture at the outlet of the flow circuit.

conditions for the occurrence of reactions in a gas phase. Vayenas et al. [41] did not examine the possibility of a heterogeneous–homogeneous mechanism of methane oxidation.

Thus, both of the groups of researchers who used FCRs with reaction mixture quenching for the direct oxidation of methane to formaldehyde noticeably improved the performance characteristics of the process under discussion. Based on a specially developed state-of-the-art technology for kinetic experiments, we considerably improved the FCR method with rapid reaction mixture quenching. Here, we describe in detail the above method and demonstrate its capabilities for studying the direct oxidation of methane to formaldehyde in the presence of both silica and other typical oxidation catalysts.

EXPERIMENTAL

Experimental Procedure

Figure 1 shows a flow chart of the FCR with reaction mixture quenching. On this basis, a flow circulation system for methane oxidation to formaldehyde was developed, which differed from its analogs [37, 41] in the following characteristics:

(a) A powerful circulation pump [42] was responsible for a high mixture circulation ratio (10000 or

higher), which allowed us to obtain a minimum methane conversion during the run of a reaction mixture through the reactor and, consequently, a maximum selectivity for formaldehyde. In this case, the residence time of the reaction mixture in the reaction volume can be as short as 0.01 s.

(b) A special quenching device [43] with water as an absorbent was responsible for the complete absorption of formaldehyde from a reaction mixture flow at the reactor outlet and the simultaneous saturation of the flow with water vapor at a specified concentration.

(c) Fundamentally new digital methane and oxygen pulse feeders allowed us to supply both large and very small flows of a starting mixture with the retention of a constant composition of this mixture [44].

The above characteristics allowed us to obtain a very high process selectivity (to 100%) for formaldehyde by varying the flow rate of the starting reaction mixture; this is the most important advantage of the method proposed over its analogs [37, 41].

The experiments were performed with a starting mixture of pure gases (99.99%) at a CH_4/O_2 volume ratio of 1 : 1. This composition of the starting mixture at 100% selectivity for formaldehyde and the complete absorption of formaldehyde in a quenching device allowed us to maintain practically the same composition of the reaction mixture over the catalyst surface at any degrees of methane conversion. With an isothermal catalyst bed and reaction volume, which can be maintained in the case of a FCR, the catalytic activity can be measured in accordance with the accurate kinetic definition of this parameter as a steady-state rate of reaction at specified temperature and composition of the contact reaction mixture [34]. This provides an opportunity to compare unambiguously the activities of various catalysts in terms of not only the rate of reaction but also practically important parameters such as the integral yield of formaldehyde and the rate of formaldehyde production. We used the above parameters to characterize catalytic activity.

The methane flow rate ($v_{CH_4}^{\circ}$) in the starting mixture of the specified composition was varied within the range 0.2–1.0 l/h. The minimum throughput of the circulation pump (v_c) was 700 l/h.

A vertical quartz tube reactor 20 mm in i.d. and 250 mm in length was used for the experiments. The top part of the reactor (45 cm^3) (Fig. 1, *3*) was filled with a packing material of crushed quartz glass (2–3 mm) to top quartz grate *5* in order to heat the feed reaction mixture. A catalyst was placed on bottom quartz grate *6* (Fig. 1). The reaction was performed at 600–770°C. The volume of the reaction zone (Fig. 1, *4*) with a specified constant temperature within the above range was 15 cm^3 at the flow rate of the starting mixture v° = 0.4–2.0 l/h. The temperature of the reaction volume was monitored with thermocouple *2* placed in a quartz tube arranged at the center of the reactor. The pressure of the reaction mixture in the reactor was ~1 bar.

The test procedure included a few operations. Initially, the reaction volume (Fig. 1, *4*) with a catalyst sample (or empty) was heated at 750°C in a flow of oxygen for 1 h; then, the temperature was decreased to 500°C and O_2 was replaced with a gas mixture of CH_4 + O_2. After attaining a specified concentration of CH_4 (50 vol %) in the initial reaction mixture, the temperature was rapidly (in 5–10 min) increased to a specified value and the reaction was performed for 1–2 h. The careful maintenance of the above sequence of operations in the test procedure allowed us to exclude the risk of inflammation of a methane–oxygen gas mixture.

In almost all cases, CH_4, CO, CO_2, and CH_2O were the main carbon-containing components of a mixture at the reactor outlet. Only in a few experiments were C_2H_6 and C_2H_4 detected among the reaction products. All of the carbon-containing compounds other than formaldehyde were determined using an LKhM-80 gas chromatograph equipped with an automated gas-sampling system. Analysis for CH_4, CO, and CO_2 was performed with the use of a separation column with SKT activated carbon (1 m × 2 mm; 100°C), which was connected in series with a methanation column (Ni/Al$_2$O$_3$; 350°C) and a flame-ionization detector (carrier gas, H$_2$; analysis time, 1 min). If required, the presence of C_2H_6 and C_2H_4 in the reaction products was monitored using a column with Porapak QS (4 m × 2 mm; 70°C) and a thermal-conductivity detector (carrier gas, He; analysis time, 9 min). The analysis of the final gas mixture in the course of the reaction demonstrated that a steady state was rapidly established (in 10–15 min) under chosen process conditions. At the end of a test, the flow rate of the final reaction gas mixture (*v*) was measured.

The resulting formaldehyde was trapped in an absorber with water [43] at room temperature. The absorber was connected to the reactor with a quartz tube. The space volume between the reaction zone and the quenching zone was ~2 cm^3. The aqueous solutions of formaldehyde did not reach stationary concentrations (at which noticeable product losses can occur because of the release of formaldehyde from solution to the gas phase [45]) during the experiment time because of the very large absorbent volume (350 ml). The amount of formaldehyde in a condensate was determined by chemical analysis using a reaction with Na$_2$SO$_3$ [46]. The rate of formaldehyde formation (*w*, mol/h) was determined from the equation

$$w = \frac{0.1N}{1000}\left(\frac{ab}{cd}\right),$$

where *N* is the normal concentration of an acid (HCl) used for titration, mol/l; *a* is the total amount of the test formaldehyde solution, ml; *b* is the amount of an acid consumed for titration, ml; *c* is the amount of the titrated formaldehyde solution, ml; *d* is the time of formaldehyde trapping, h.

As mentioned above, many researchers [19, 25, 33] noted a positive effect of the addition of water vapor to the reaction mixture on selectivity for formaldehyde. Stadnik and Gomonai [19] and Yu et al. [25] explained this phenomenon by the fact that water vapor cooled and carried formaldehyde molecules from a hot reaction zone, whereas Berndt et al. [33] related the positive effect of water vapor to the generation of additional active sites on the surface of catalysts. In this work, an absorber with water also saturated the reaction mixture with water vapor at 20–25°C, that is, to a partial vapor pressure of 0.024–0.032 bar simultaneously with form-aldehyde trapping. Special experiments demonstrated that an increase in the saturator absorber temperature to 40°C and, correspondingly, the doubling of the partial pressure of water vapor in the reaction mixture (to 0.075 bar) under the conditions of our experiments had no effect on the yield of formaldehyde and the distribution of reaction products. However, the freezing of water vapor from the reaction mixture with the use of a trap (–20°C) mounted at the saturator absorber outlet decreased the integral yield of and selectivity for form-aldehyde by 20–30%.

The integral yield Y (the molar percentage of CH_4 converted into CH_2O during the run of a starting reaction mixture through a FCR circuit with consideration for circulation) and the selectivity S_{CH_2O} for formaldehyde, as well as the selectivities (S_i) for CO (S_{CO}) and CO_2 (S_{CO_2}) and the integral conversion of methane (X), were calculated from the equations

$$Y = \frac{w \times 22.4 \times 100}{v^\circ_{CH_4}}, \quad S_{CH_2O} = \frac{w \times 22.4 \times 100}{v^\circ_{CH_4} - (m_{CH_4} v)},$$

$$S_i = \frac{m_i v \times 100}{v^\circ_{CH_4} - (m_{CH_4} v)}, \quad \text{and} \quad X = \frac{Y \times 100}{S_{CH_2O}},$$

where $v^\circ_{CH_4}$ is the methane flow rate in the starting reaction mixture, l/h; v is the flow rate of the final reaction mixture, l/h; m_{CH_4} is the mole fraction of methane in the final reaction mixture; m_i is the mole fraction of CO or CO_2 in the final reaction mixture. Note that the real yield of formaldehyde and the degree of methane conversion during the run of a reaction mixture through the reactor were much lower than the calculated integral values and equal to Y/n and X/n, respectively, where $n = v_c/v$ is the mixture circulation ratio.

Materials

In this study, two types of silica materials (quartz glass and glass cloth) and several typical catalysts for oxidation processes were used as catalysts.

The samples of quartz glass (hollow tubes, cylinders, and irregularly shaped crushed pieces) exhibited low specific surface areas ($S_{sp} < 0.1$ m²/g), which were

measured using the BET method from the thermal desorption of argon; these specific surface areas were close to the outer geometric surface areas of the samples.

In terms of structure, quartz glass is a continuous network of silicon–oxygen tetrahedrons linked by siloxane bonds. Low specific surface areas and high preparation temperatures (1800°C) of quartz glass suggest very low concentrations of hydroxyl groups on the surface of such catalysts. The chemical analysis of glass performed by X-ray fluorescence spectroscopy demonstrated that the main component of this glass (~99.5 wt %) was SiO_2. The concentrations of impurities, in particular, Cu and Fe, were no higher than the instrument background (<0.01%).

The SSB-20 silica glass cloth was prepared by the acid extraction (leaching) of nonsilica components from commercial sodium aluminosilicate glass cloth (PO Steklovolokno, Polotsk, Belarus) followed by the calcination of the leached sample in air at 300°C. In terms of chemical composition, the leached glass cloth was almost pure silicon dioxide with trace impurities of Al (0.53 wt %), Na (0.05 wt %), and Fe (<0.01 wt %). The matrix formed upon leaching was similar to the fused silica samples used in this work in terms of chemical composition; however, it was essentially different from traditional silica materials in properties [47]. Its structure and properties were most adequately described by a pseudolayered intercalation structure model. This model includes the alternating layers of several silicon–oxygen tetrahedrons separated by narrow (<4 Å) voids with a large amount of OH groups (~5000 µmol/g), which are much different from the surface hydroxyl groups of ordinary globular silicas in properties.

The test sample of the SSB-20 glass cloth was a woven twill fabric made of microfibers ~7 µm in diameter spun in threads ~0.5 mm in diameter. For the glass cloth, S_{sp} ~1 m²/g, which corresponds to the geometric surface area of cylindrical microfibers ~7 µm in diameter. The samples as cloth pieces or threads from this cloth were placed in the reactor.

The silica materials chosen allowed us to vary widely the contact surface (S) and free volume (V) in the reaction zone and the shape of the free volume. The values of S and V were determined by calculations. To calculate the volume occupied by a quartz material, the true density of quartz $\rho = 2.2$ g/cm³ was used.

In the series of experiments with catalysts, AShNTs-3 and IK-1-4 commercial catalyst samples, as well as catalysts based on the above silica glass cloth (samples K_1, K_2, and K_3), were used. To perform catalytic tests, the parent granules of AShNTs-3 and IK-1-4 commercial catalysts were crushed and a fraction of 2–3 mm was used. The samples of glass cloth catalysts were loaded as threads 0.5 mm in diameter. In terms of chemical composition, the granular cracking catalyst AShNTs-3 (OAO Ufimskii NPZ) was a synthetic aluminosilicate containing synthetic zeolite Y with Na_2O (0.7%) and

Table 1. Changes in *S*, *V*, and *S/V* on filling a reaction volume with various silica packing materials

Entry	Reaction volume loading	S, cm^2	V, cm^3	S/V, cm^{-1}
1	Empty	40	15.0	3
2	Tubes (d_1 = 5 mm, d_2 = 3 mm, l = 5 mm)	160	9.5	17
3	Crushed quartz (2–3 mm)	140	7.5	19
4	Cylinders (d = 3.5 mm, l = 4 mm)	200	6.0	30
5	Crushed quartz (1–2 mm)	300	7.0	40
6	SSB-20 (threads, 0.15 g)	1500	14.9	100
7	SSB-20 (threads, 1.5 g)	15 000	14.3	1000
8	SSB-20 (cloth, 3.6 g)	36 000	13.3	2700

Fe_2O_3 (0.2%) impurities. The catalyst IK-1-4 (PO Minudobreniya, Voskresensk, Russia) for sulfur dioxide oxidation to sulfur trioxide was a mixture of potassium and sodium oxosulfatovanadates supported on silicon dioxide. In terms of oxides, its averaged composition corresponds to 7.5% V_2O_5, 11% K_2O, 2% Na_2O, 20% SO_3, and the balance SiO_2. The specific surface area of this catalyst was 7 m^2/g. At temperatures higher than 400°C, oxosulfatovanadates occurred as a melt distributed over the silica gel surface. Catalysts K_1 (0.02 wt % V) and K_2 (0.66 wt % V) based on glass cloth were prepared by impregnating the glass cloth with a solution of ammonium metavanadate. Sample K_3 (0.03 wt %) was prepared by impregnating the glass cloth with a solution of $Pt(NH_3)_4Cl_2$. All of the impregnated samples were dried at 110°C and calcined in air at 300°C. The sample containing platinum was reduced in hydrogen at 200°C for 1 h after calcination.

RESULTS AND DISCUSSION

As mentioned above, formaldehyde is unstable at a high temperature in a gas phase, particularly, in an oxidizing atmosphere. According to published data [48, 49], the quasi-unimolecular rate constants of homogeneous formaldehyde degradation to the simpler compounds H_2 and CO even in an inert gas atmosphere at atmospheric pressure over the temperature range 600–700°C are ~10^2–10^3 s^{-1}. In a homogeneous oxygen-containing atmosphere, the rate constant of the most rapid primary bimolecular reaction

$$HCHO + O_2 \longrightarrow {}^\bullet CHO + HO_2^\bullet$$
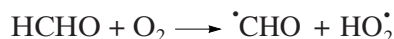
over the temperature range 400–700°C is described by the expression $10^{-10}\exp(-170 \,(kJ/mol)/RT)$ cm^3/s [50]; similar experimental data were reported by Tsang and Hampson [51]. The above rate constants indicate that, even in the absence of interactions with gas-phase species that are more reactive than O_2 and/or with the catalyst surface or reactor wall, the lifetime of the CH_2O molecule under the test process conditions (T = 750°C; P_{O_2} ~ 0.5 bar) cannot be longer than ~10^{-2}–10^{-3} s in the case of quasi-molecular degradation or ~1 s in the case of the interaction with O_2. This imposes rigid requirements on the maximum residence time of the reaction mixture in reactors for the production of formaldehyde: this time also cannot be longer than 10^{-2} s. Thus, in any case, the production of formaldehyde by the direct catalytic oxidation of methane requires the use of reactors with a very short contact time and rapid quenching of reaction products. In the case of FCRs, the residence time of a reaction mixture in the reaction volume can be estimated as $t_r = (V/v_c)(298/T)$, where V is the free reaction volume, v_c is the throughput of a circulation pump at room temperature, and T is the absolute temperature of the reaction volume. In our system, short residence times were reached at the pumping of a mixture using a circulation pump with a throughput of no less than 900–1000 l/h.

Evidently, at such short times t_r, the degree of methane conversion into formaldehyde can reach high values only at a very high catalyst activity.

To examine the oxidation of methane to formaldehyde under FCR conditions, we used various silica packing materials in order to study the effect of the reaction volume geometry on process performance characteristics. The study was performed at a reaction volume temperature of 750°C. We found in preliminary experiments that the specified reaction volume temperature remained practically unchanged under changes of packing materials. Thus, because of the complicated procedure of reactor loading, the subsequent experiments of this series were performed without placing a thermocouple pocket (quartz tube) in the reaction space except for a few experiments in an empty volume. The methane flow rate in the starting mixture ($v_{CH_4}^\circ$) and the throughput of the circulation pump (v_c) at room temperature were 0.5 and 700 l/h, respectively. Tables 1 and 2 summarize the results of this study.

Table 1 summarizes the parameters of the empty FCR reaction volume (entry 1) and the volume filled with various silica packing materials (entries 2–8), which are characterized by the contact surface area S, the free reaction volume V, and the S/V ratio. Table 2

Table 2. Changes in the performance characteristics of the process of methane oxidation to formaldehyde at 750°C depending on the size and shape of silica packing materials in the reaction volume at the pump throughput $v_c = 700$ l/h

Entry	v^o, l/h	$v^o_{CH_4}$, l/h	v, l/h	n	t_r, s	w, mmol/h	Y, %	X, %	m_{CH_4}	m_{CO}	m_{CO_2}	S_{CH_2O}, %	S_{CO}, %	S_{CO_2}, %	w_{sp}, mmol cm^{-2} h^{-1}
1	1.01	0.493	0.292	2400	0.023	9.0	40.7	72.7	0.487	0.047	0.011	56.0	3.9	0.9	200
2	0.99	0.501	0.308	2300	0.015	11.2	50.0	68.2	0.493	0.120	0.167	73.3	11.0	15.0	70
3	1.01	0.500	0.470	1500	0.012	8.6	38.4	54.1	0.433	0.073	0.106	71.0	13.0	18.0	60
4	1.01	0.493	0.609	1150	0.009	5.6	25.5	40.7	0.477	0.045	0.065	62.6	13.7	19.8	30
5	1.01	0.492	0.580	1200	0.012	5.0	22.9	43.7	0.393	0.057	0.126	52.4	15.3	34.0	20
6	1.02	0.500	0.260	2700	0.023	8.4	37.7	76.2	0.446	0.095	0.114	49.5	6.6	7.8	6
7	1.03	0.517	0.472	1500	0.020	7.0	30.4	54.1	0.425	0.088	0.19	56.2	14.8	31.9	5
8	1.02	0.517	0.675	1000	0.020	3.5	15.2	33.4	0.465	0.016	0.137	45.5	5.7	52.4	1

Note: v^o is the flow rate of the starting reaction mixture; $v^o_{CH_4}$ is the flow rate of methane in the starting reaction mixture; v is the flow rate of the reaction mixture at the outlet of the flow circuit; $n = v_c/v$ is the reaction mixture circulation ratio; $t_r = (V/v_c)(298/T)$ is the residence time of the mixture in the reaction volume during a run through the reactor; m_i is the mole fraction of CH_4, CO, or CO_2 in the final reaction mixture; $w_{sp} = w/S \times 10^{-3}$ is the specific pseudoheterogeneous rate of formaldehyde formation; entries are specified in Table 1.

gives the kinetic characteristics of the process depending on the parameters of the FCR reaction volume corresponding to filling conditions specified in Table 1 (entries 1–8).

Data in Tables 1 and 2 indicate that the organization of a reaction volume exerts a considerable effect on the process characteristics of methane oxidation to formaldehyde and hence support a homogeneous–heterogeneous mechanism of this process. Let us consider the experimental results in more detail.

As can be seen in Table 2, the oxidation of methane in an empty reaction volume (experiment no. 1) occurred with sufficiently high values of Y and S_{CH_2O} and low values of S_{CO} and S_{CO_2}. (Unfortunately, the effect of the surface of the bottom heat-exchange packing bed in reactor zone 3 and/or a separating grate, where the temperature is close to the temperature of zone 4, cannot be excluded because of the necessity of preheating the initial reaction mixture.) In this experiment, as well as in experiment no. 6, small amounts of C_2H_6 and C_2H_4 (total <10 vol %) were detected. Detailed analysis for C_2 products was not performed. In all of the other cases, the formation of C_2 hydrocarbons was not observed; an imbalance on carbon in the reactants and products was no higher than ±10% including measurement error. The process in an empty volume was unsteady with temperature fluctuations within the limits of about 100°C; in reproduced experiments, the process was occasionally accompanied by one or two light flashes. The experiment resulted in the rupture of a membrane in the circulation pump. Previously, Gomonai [23, 37] observed a self-oscillating regime in the oxidation of methane to formaldehyde. Non-steady-state phenomena of this kind accompanied by a dra-

matic increase in the rate of reaction and light emission flashes are known as cold flames and characteristic of the radical-chain gas-phase oxidation of methane [3].

As can be seen in Table 2, in all of the experiments, the composition of the reaction mixture in a flow circuit after formaldehyde absorption was found to be uniform. In general, the mixture contained only relatively small amounts (to ~10–20 vol %) of CO and CO_2 in addition to CH_4 and O_2. It is believed that, to a first approximation, these additives have no considerable effect on the main test process. This allows us to make conclusions on the direct effect of packing material in the reaction volume on the process of methane oxidation.

It is well known that the area and nature of a contact surface play an important role in the kinetics of chain gas-phase reactions. On the one hand, the surface can initiate the appearance of active intermediates (such as atoms and/or free radicals) in a chain reaction; on the other hand, it participates in chain termination. Semenov [52] noted a strong effect of vessel sizes and the state of vessel walls on the rate of methane oxidation with oxygen. In this case, the rate of reaction in a vessel packed with quartz tubes or beads was always much lower than that in an empty reactor.

Our experimental results suggest a complex character of the effect of the quartz surface and free volume on the kinetics of methane oxidation to formaldehyde. Thus, on packing the empty reaction volume with quartz tubes (Table 1, entry 2), the value of V decreased and S increased; correspondingly, the S/V ratio increased. However, in this case, the values of Y and S_{CH_2O} (Table 2, entry 2) increased rather than decreased. It is clear that the total free volume V is combined of smaller volumes, whose shapes and sizes

depend on the shape and size of the packing material. In the case of tubes, there are wider voids between external tube boundaries and smaller voids within the tubes. It is likely that free voids with such sizes and shapes are favorable for the occurrence of formaldehyde formation reactions in the gas phase, and they prevent its oxidation; according to Margolis et al. [21], this oxidation occurs by ~90% in the volume in the presence of SiO_2. This hypothesis can be supported by well-known data [53] on the strong inhibition of the rate of oxidation of gaseous formaldehyde upon a narrowing of the reaction space. In experiment no. 3 (Tables 1, 2), as compared with experiment no. 2, the value of S changed only slightly, as well as the S/V ratio; however, the free volume (V) changed more noticeably. It is of interest that the yield of formaldehyde decreased in the same manner, whereas selectivity for formaldehyde remained almost unchanged; the selectivities S_{CO} and S_{CO_2} changed only slightly. It is believed that, in experiments with similar values of S and S/V, the value of Y (and X) mainly depends on the value of V. A comparison of experiment nos. 4 and 5 (Tables 1, 2) indicates that, at similar values of V, the values of Y (and X) were also similar; it is likely that selectivity changes were due to changes in the contact surface area (S). In general, a smooth increase in the S/V ratio for quartz packing materials (Tables 1, 2, entries 2–5) resulted in a gradual decrease in Y and S_{CH_2O}, a weak increase in S_{CO}, and a more noticeable increase in S_{CO_2}. This effect of the S/V ratio on kinetics is typical of heterogeneous–homogeneous processes [54]. Finally, homogeneous gas-phase reactions become completely suppressed at a sufficiently high value of this ratio and the process changed to purely heterogeneous conditions [32, 35, 36].

The SSB-20 glass-cloth packing materials of (Tables 1, 2, entries 6, 7) allowed us to increase dramatically S and the S/V ratio in the reaction volume. However, as compared with experiment no. 5 (crushed quartz), the values of Y and S_{CH_2O} did not decrease in this case. On the contrary, in experiment no. 6 with the addition of glass-cloth fibers, higher values of Y and S_{CH_2O}, which were close to Y and S_{CH_2O} obtained in experiment no. 1 (empty reactor), were obtained. As in the course of reaction in an empty volume, C_2 hydrocarbons were detected in the reaction products; however, carbon oxides were formed in larger amounts and phenomena related to a change of the process to a self-oscillating mode were not observed. It is likely that the observed similarity between the courses of the processes in the above two cases is due to the fact that the total value of V remained practically unchanged upon the addition of fibers to the empty reaction volume. At the same time, fibers divided the free space into a number of smaller cavities and thereby increased the surface effect on chain reactions. An increase in the number of fibers in the reaction space (experiment no. 7) addition-

ally decreased the size of cavities that constitute the free volume, the total value of which (V) did almost not decrease in this case. The integral yield of formaldehyde (Y) also decreased only slightly, whereas selectivities for carbon oxides, particularly S_{CO_2}, noticeably increased. In the case of filling the reaction volume with glass cloth pieces (Tables 1, 2, entry 8), the surface effect on product distribution in favor of carbon oxides became even greater.

Table 2 summarizes the rates of formaldehyde formation w referenced to the surface area (S) of a silica packing material represented as the specific pseudoheterogeneous rate of formaldehyde formation (w_{sp}). These data clearly indicate that, under conditions of our experiments, the formation of formaldehyde occurred in the gas phase rather than on the surface of silica because the values of w_{sp} decreased with increasing surface area. At the same time, in the purely heterogeneous oxidation of methane (Stadnik and Gomonai [20] believed that it was achieved), the amount of formaldehyde formed in the process was proportional to the surface area of quartz.

The study of the effect of the organization of a reaction volume on the kinetics of methane oxidation to formaldehyde allowed us to make a few conclusions.

(1) The size and shape of the silica packing material are responsible for the size and shape of free voids within the reaction space.

(2) The total free volume (V) is the main parameter responsible for the integral yield of formaldehyde (Y). This is due to the fact that the residence time of a mixture in the reaction volume and, correspondingly, the conversion time of the reaction mixture in a reactor are proportional to V.

(3) The contact surface area (S) affects the distribution of reaction products. The higher the values of S and the S/V ratio and the smaller the voids that constitute the free reaction volume, the higher selectivities for the formation of carbon oxides by undesirable reaction paths because of the higher probability of further formaldehyde oxidation.

The relationship of the reaction kinetics with the residence time (t_r) (Table 2) and the assumed nature of the effect of the contact surface area on selectivity for products will be considered in more detail below.

It was of interest to study the temperature dependence of the rate of formaldehyde formation under reaction volume packing conditions that provide optimum performance characteristics of the process. For this purpose, we studied the reaction of methane oxidation at 600–770°C and initial reaction mixture flow rates of 0.4, 0.9, and 2.0 l/h with the filling of the reaction volume with quartz tubes.

The experiments were performed under continuous temperature control in the reaction volume, the S, V, and S/V parameters of which were 170 cm^2, 7.5 cm^3, and 20 cm^{-1}, respectively, with consideration for a thermo-

Table 3. Rate of formation (w) and the integral yield (Y) of formaldehyde and selectivity for formaldehyde (S_{CH_2O}) in the reaction of methane oxidation depending on the temperature of the reaction volume filled with quartz tubes

Experiment no.	T, °C	$v^\circ_{CH_4}$, l/h	v°, l/h	v, l/h	n	t_r, s	w, mmol/h	Y, %	$S^*_{CH_2O}$, %
1	600	0.196	0.406	0.374	2400	0.0102	0.70	8.0	98
2	610	0.196	0.396	0.352	2600	0.0101	0.87	9.9	98
3	630	0.199	0.438	0.339	2700	0.0099	2.10	23.7	96
4	650	0.200	0.420	0.232	3900	0.0097	4.20	47.0	100
5	700	0.200	0.410	0.105	8600	0.0092	7.00	78.4	100
6	740	0.207	0.420	0.065	14000	0.0088	8.05	86.8	100
7	750	0.200	0.418	No	>14000	0.0087	8.70	98.0	100
8	600	0.446	0.929	0.899	1000	0.0102	0.70	3.5	100
9	640	0.470	0.970	0.908	1000	0.0098	1.40	6.7	100
10	680	0.445	0.930	0.799	1100	0.0093	2.80	14.1	96
11	730	0.467	0.957	0.700	1300	0.0089	5.60	26.9	98
12	730	0.440	0.900	0.655	1400	0.0089	5.30	27.0	97
13	750	0.432	0.904	0.547	1600	0.0087	7.70	40.0	97
14	770	0.434	0.931	0.376	2400	0.0086	11.20	58.0	90
15	650	1.182	2.452	2.350	380	0.0097	2.10	4.0	93
16	700	0.945	2.010	1.720	520	0.0092	6.30	14.9	97
17	750	0.942	2.000	1.580	570	0.0087	9.00	21.0	96

Note: v°, $v^\circ_{CH_4}$, v, n, and t_r are specified in Table 2.

 * The accuracy in the determination of S was ±10%.

couple pocket. The throughput of a pump (v_c) was 900 l/h. The residence time of a reaction mixture in the reaction volume was determined as $t_r = (V/v_c)(298/T)$ with a correction for temperature. Under the conditions chosen, t_r was about 0.01 s (Table 3). The residence time t_r is an integrated quantity because, on the introduction of a quartz packing material, the free reaction volume consists of smaller volumes whose sizes depend on the size of the packing material. In a number of cases, these volumes form pockets with stagnant zones for the migration of the reaction mixture and hence longer conversion times [55]. Selectivity for formaldehyde was found from the equation

$$S_{CH_2O} = \frac{w \times 22.4 \times 100}{(v^\circ - v)/2}.$$

In all of the experiments, the imbalance on carbon was no higher than the measurement error of ±10%. Table 3 and Fig. 2 show the results of the study.

In Table 3, it can be seen that the selectivity of the process for formaldehyde S_{CH_2O} was close to 100% under the conditions chosen (t_r of no longer than 0.01 s); in this case, $X \cong Y$. At 600°C, the rates of formaldehyde formation were very low, and they were practically indistinguishable at the flow rates of the initial reaction mixture equal to 0.4 and 0.9 l/h. This is consis-

tent with well-known data [19, 24] on the high temperature of the onset of noticeable methane oxidation on SiO_2. The rate of formaldehyde formation (w) increased with temperature at all of the tested flow rates
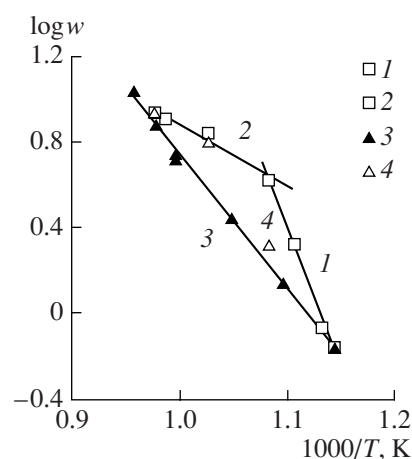

Fig. 2. The temperature dependence of the rate of formaldehyde formation in the oxidation of methane in a reaction volume packed with quartz tubes at the flow rates of the initial reaction mixture of (1, 2) 0.4, (3) 0.9, and (4) 2.0 l/h. The initial reaction mixture contained CH_4 and O_2 (1 : 1, by volume).
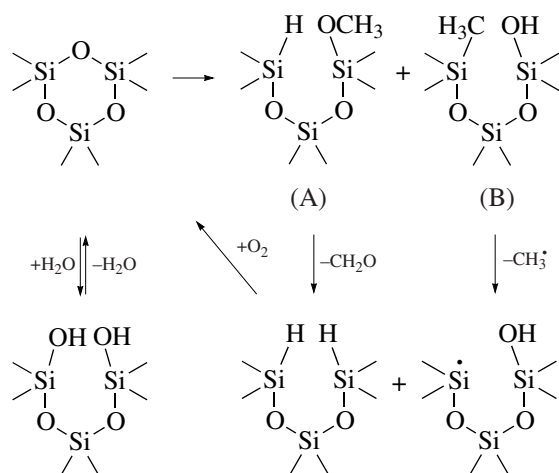
Fig. 3. Schematic diagram of the surface dehydroxylation of silica and methane activation at reactive siloxane sites with the release of formaldehyde and methyl radicals into the gas phase (according to Sun et al. [14]).

of the initial reaction mixture ($v°$). Because formaldehyde was trapped in an absorber and removed from the reaction mixture, this resulted in a decrease in the volume of the mixture and, consequently, a decrease in the space velocity of the final reaction mixture (v); correspondingly, the circulation ratio (n) increased. At $T = 750°C$ and $v°_{CH_4} = 0.2$ l/h ($n > 10000$), methane was almost completely converted into formaldehyde.

Figure 2 shows the temperature dependence of the rate of formaldehyde formation for the tested flow rates (0.4, 0.9, and 2.0 l/h) of the initial reaction mixture in accordance with data obtained in experiment nos. 1–7, 8–14, and 15–17 (Table 3).

The Arrhenius function obtained at an initial mixture flow rate of 0.4 l/h ($v°_{CH_4} = 0.2$ l/h) can be separated into two portions. Straight line *1* for the $\log w - 1/T$ relationship ($T = 600–650°C$; $n = 2000–4000$) corresponds to the apparent activation energy (E_a) of formaldehyde formation equal to 229 kJ/mol. This activation energy is consistent with $E_a = 230$ kJ/mol for the formation of CH_2O on quartz, which was experimentally obtained by Stadnik and Gomonai [19], and close to $E_a = 254 \pm 18$ kJ/mol for the thermal degradation reaction of methoxy groups ($\equiv Si–O–CH_3$) on the surface of SiO_2 [15] with the release of CH_2O. Straight line *2* (Fig. 2) for the $\log w - 1/T$ relationship corresponds to $E_a = 61$ kJ/mol, which is much lower than the above values of E_a for the formation of CH_2O on the surface of SiO_2. This suggests a change in the rate-determining reaction steps on going to the temperature region above 650°C.

Based on experimental data and current concepts of CH_4 activation on the surface of SiO_2 [14, 15], we assume that the dehydroxylation of the surface of silica (reactor walls and packing material) with the formation of reactive siloxane sites occurred in the course of training the reaction volume (empty or filled with a packing material) in a flow of O_2 at a high temperature (750°C). The reaction scheme shown in Fig. 3, which was considered in detail by Sun et al. [14], illustrates the interaction of these sites with methane. We found that the elimination of the stage of high-temperature training in oxygen (or nitrogen) from the experimental procedure resulted in a dramatic decrease in the rate of formaldehyde formation.

The apparent activation energy $E_a = 229$ kJ/mol obtained for $v° = 0.4$ l/h at $T = 600–650°C$ and $t_r = 0.01$ s ($n = 2000–4000$) suggests that the rate of methane oxidation under these conditions depends on heterogeneous stage A of the thermal decomposition of surface methoxy-containing complexes. According to quantum-chemical calculations [15], the following hypothetic reaction of the thermal degradation of methoxy groups is strongly endothermic:
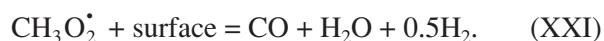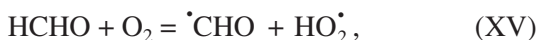
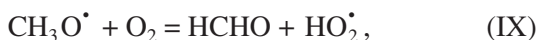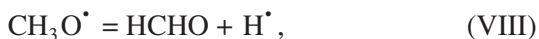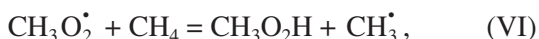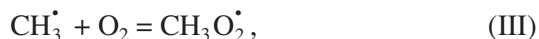$$\equiv Si–O–CH_3 \longrightarrow \equiv SiH + CH_2O. \qquad (I)$$

This is responsible for the high values of experimentally observed temperature and activation energy of degradation of these groups. According to IR-spectroscopic data [15], reaction (I) did not occur to a noticeable degree at temperatures lower than 600°C; this is consistent with our data. Note that Brei et al. [15] determined E_a for reaction (I) from thermal desorption curves under conditions of low pressures, when the thermal activation of surface methoxy groups mainly occurred (according to Brei et al. [15]) by energy transfer from a SiO_2 matrix. It is likely that the value of E_a (229 kJ/mol) for the formation of CH_2O under steady-state conditions was lower than that published by Brei et al. [15] because of the overall exothermicity of elementary steps preceding the rate-limiting step (I) (e.g., see [56, 57]).

At temperatures higher than 650°C (Fig. 2, straight line *2*), the apparent activation energy decreased several times to $E_a = 61$ kJ/mol. The value of E_a in segment *2* is higher than the published value of 32.6 kJ/mol [58] obtained for the E_a of CH_2O formation in a homogeneous gas-phase reaction of methane oxidation. It is believed that, at temperatures of about 650°C, intermediate complexes like B on the surface of quartz began to decompose with the desorption of methyl groups into the volume; this is a new radical-chain reaction path for the formation of formaldehyde due to free-radical reactions. Moreover, the radical centers $\equiv Si–O^{\bullet}$ resulting from the degradation of complexes B can also interact with methane in the following reaction with the formation of $CH_3^{\bullet}$ free radicals [3]:

$$\equiv Si–O^{\bullet} + CH_4 \longrightarrow \equiv Si–OH + CH_3^{\bullet}. \qquad (II)$$

Because the $CH_3^{\bullet}$ radicals can escape into the bulk, of interest is the model suggested by Baldwin et al. [9] for the uncatalyzed activation of methane in the gas phase at medium pressures. This model includes the most important radical reactions yielding partial oxidation products, in particular, formaldehyde. In accordance with this model, the appearance of $CH_3^{\bullet}$ free radicals in the bulk initiated a sequence of the reactions given below:

$$CH_3^{\bullet} + O_2 = CH_3O_2^{\bullet}, \tag{III}$$

$$CH_3O_2^{\bullet} = HCHO + HO^{\bullet}, \tag{IV}$$

$$CH_4 + HO^{\bullet} = CH_3^{\bullet} + H_2O, \tag{V}$$

$$CH_3O_2^{\bullet} + CH_4 = CH_3O_2H + CH_3^{\bullet}, \tag{VI}$$

$$CH_3O_2H = CH_3O^{\bullet} + HO^{\bullet}, \tag{VII}$$

$$CH_3O^{\bullet} = HCHO + H^{\bullet}, \tag{VIII}$$

$$CH_3O^{\bullet} + O_2 = HCHO + HO_2^{\bullet}, \tag{IX}$$

$$CH_4 + HO_2^{\bullet} = CH_3^{\bullet} + H_2O_2, \tag{X}$$

$$HCHO + CH_3^{\bullet} = {}^{\bullet}CHO + CH_4, \tag{XI}$$

$$HCHO = {}^{\bullet}CHO + H^{\bullet}, \tag{XII}$$

$$HCHO + H^{\bullet} = H_2 + {}^{\bullet}CHO, \tag{XIII}$$

$$HCHO + HO^{\bullet} = {}^{\bullet}CHO + H_2O, \tag{XIV}$$

$$HCHO + O_2 = {}^{\bullet}CHO + HO_2^{\bullet}, \tag{XV}$$

$$HCHO + HO_2^{\bullet} = {}^{\bullet}CHO + H_2O_2, \tag{XVI}$$

$$H_2O_2 = 2HO^{\bullet}, \tag{XVII}$$

$${}^{\bullet}CHO + O_2 = CO + HO_2^{\bullet}, \tag{XVIII}$$

$$CO + HO^{\bullet} = CO_2 + H^{\bullet}, \tag{XIX}$$

$$CO + HO_2^{\bullet} = CO_2 + HO^{\bullet}, \tag{XX}$$

$$CH_3O_2^{\bullet} + surface = CO + H_2O + 0.5H_2. \tag{XXI}$$

In accordance with the above reaction scheme, formaldehyde is a primary molecular product of a number of free-radical reactions. In the case of the kinetic irreversibility of formaldehyde formation, the subsequent transformations of this compound in a gas phase result in the formation of CO and CO_2. Taking into account that our data (Table 3) were obtained at $S_{CH_2O} = 100\%$ and formaldehyde was the only carbon-containing product of partial oxidation, we assumed that the main reaction path of CH_2O formation in the temperature range 650–750°C at $v^{\circ} = 0.4$ l/h can be due to reactions (III)–(V). Nevertheless, the rates of these reactions and the concentrations of corresponding radicals

evaluated previously by Semenov [52] allowed the author to hypothesize that the chain propagation of free-radical methane oxidation in the a gas phase at atmospheric pressure is determined by the reaction

$$CH_3^{\bullet} + O_2 = HCHO + HO^{\bullet}, \tag{IIIa}$$
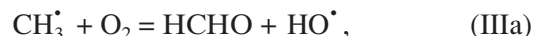
whereas chain termination is due to the recombination of $HO^{\bullet}$ radicals on the surface. As estimated by Arutyunov and Krylov [3], reaction (V) makes a considerable contribution (>90%) to methane oxidation at low pressures. Reaction (IIIa) is the sum of reactions (III) and (IV). The apparent activation energy of this overall reaction (63 kJ/mol [59]) is consistent with the apparent activation energy of 61 kJ/mol obtained in this work for methane oxidation to formaldehyde at 650–750°C and $v^{\circ} = 0.4$ l/s ($t_r = 0.01$ s) under steady-state process conditions in the reaction volume packed with quartz tubes. It is believed that, under the specified conditions, the process of methane oxidation mainly occurred by a nonbranched radical-chain mechanism, as evidenced by the observed linear relationship between $\log w$ and $1/T$ [52]. Possible reactions (XI)–(XVI) did not participate in the development of the chain process because of the short residence time of the reaction mixture in the reaction volume and the complete removal of formaldehyde from the hot zone. This allowed us to reach almost 100% methane conversion into formaldehyde at 750°C (Table 3). It is likely that the lower value of E_a (32.6 kJ/mol) obtained by Karmilova et al. [58] was due to the considerable effect of the pretreatment of reactor walls with HF on the overall process. The high sensitivity of gas-phase free-radical chain processes to the state of the contact surface is well known.

At $v^{\circ} = 0.9$ l/h ($v^{\circ}_{CH_4} = 0.45$ l/h) and $t_r = 0.01$ s ($n < 2000$), the Arrhenius function (Fig. 2, straight line 3) corresponds to the apparent activation energy $E_a = 120$ kJ/mol. This value is close to $E_a = 125 \pm 15$ kJ/mol for the formation of formaldehyde in methane oxidation in a quartz tube ($V = 3$ cm^3) at $T = 500–600°C$ and $t_r \sim 3–4$ s [12]. Note that Kastanas et al. [12] detected a deviation from the Arrhenius law at temperatures higher than 600°C. The value of $E_a = 120$ kJ/mol obtained in this work is lower than $E_a = 229$ kJ/mol for the heterogeneous initiation of formaldehyde formation but higher than $E_a = 61$ kJ/mol for the formation of CH_2O in the volume at $v^{\circ} = 0.4$ l/h (Fig. 2, segment 2).

It is believed that, as the feed rate of the starting mixture (v°) is increased, the homogeneous component of the process becomes predominant over the entire temperature range above 600°C because of the effective activation of surface complexes B with the escape of $CH_3^{\bullet}$ free radicals into the bulk; the free-radical reaction chain length also increases. In this case, the probability of other radical reactions, such as the reaction
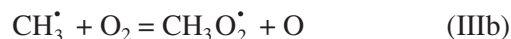
$$CH_3^{\bullet} + O_2 = CH_3O_2^{\bullet} + O \tag{IIIb}$$

Table 4. Activation energies of elementary steps in the formation of formaldehyde in the gas phase [59]

Reaction no.	Reaction	E_a, kJ/mol
(IIIa)	$CH_3^\bullet + O_2 \longrightarrow HCHO + HO^\bullet$	63.00
(V)	$CH_4 + HO^\bullet \longrightarrow CH_3^\bullet + H_2O$	11.25
(VI)	$CH_3O_2^\bullet + CH_4 \longrightarrow CH_3O_2H + CH_3^\bullet$	90.30
(VII)	$CH_3O_2H \longrightarrow CH_3O^\bullet + HO^\bullet$	179.91
(VIII)	$CH_3O^\bullet \longrightarrow HCHO + H^\bullet$	140.00
(IX)	$CH_3O^\bullet + O_2 \longrightarrow HCHO + HO_2^\bullet$	10.88
(X)	$CH_4 + HO_2^\bullet \longrightarrow CH_3^\bullet + H_2O_2$	89.96
(IIIb)	$CH_3^\bullet + O_2 \longrightarrow CH_3O^\bullet + O$	129.00
(IIIc)	$O + CH_4 \longrightarrow CH_3^\bullet + HO^\bullet$	35.50
(IIId)	$HO^\bullet + surface$	0
(IIIe)	$HO_2^\bullet + HO_2^\bullet \longrightarrow H_2O_2 + O_2$	0

Note: The numbering of reactions (V)–(X) corresponds to the scheme proposed in [9].

and the subsequent reactions, also increases. Anyway, Vedeneev et al. [59] reported the value E_a = 129 kcal/mol for elementary reaction (IIIb). It is likely that this reaction is the rate-limiting step of formaldehyde formation at $v° = 0.9$ l/h and $T = 600–770°C$ under conditions of $t_r = 0.01$ s. In this case, the $\log w – 1/T$ relationship is also described by a straight line, which suggests that chains are insignificantly branched under the specified oxidation reaction conditions [52].

However, as the feed rate of the starting mixture is further increased to $v° ~ 2.0–2.5$ l/h (Table 3), the $\log w − 1/T$ plot exhibited a deviation from the Arrhenius law (Fig. 2, points 4) due to an increase in chain lengths and, likely, chain branching, the probability of which increased with temperature [52]. Indeed, at $T = 750°C$, a gas flow after the absorber was absent in the first 10–15 min of the reaction; this suggested the complete conversion of methane into formaldehyde. It is likely that, during this period, the rate of formaldehyde formation reached a maximum value of 42 mmol/h for $v° = 2.0$ l/h (Table 3). Then, after two plops and flashes, a flow of the final gas mixture appeared and the process changed from unstable to steady-state conditions. In this case, the rate of formaldehyde formation dramatically decreased, as compared with the initial rate; the value of w averaged over a 1-h test was 9 mmol/h.

Thus, even under conditions of filling the reaction volume with quartz tubes and 100% selectivity for formaldehyde at $t_r = 0.01$ s, the oxidation process can occur by a branched-chain mechanism with the appearance of critical phenomena as the temperature and the

feed rate of the starting mixture of $CH_4 + O_2$ are increased.

The experimental results obtained in this work unambiguously suggest that the oxidation of methane to formaldehyde at temperatures higher than 600°C in the presence of a heterogeneous packing material of SiO_2 occurs by a heterogeneous–homogeneous mechanism. A considerable advantage of the improved FCR method is the possibility of separately studying the part of the process responsible for the formation of the target product at the early steps of a complex process by using short residence times t_r.

With consideration for the experimental results, it is of interest to consider in detail a set of gas-phase reactions initiated by $CH_3^\bullet$ radicals leading to formaldehyde formation. Table 4 summarizes the published values [59] of E_a for gas-phase free-radical reactions, which seem important for the occurrence of the overall process under discussion.

As mentioned above, it is likely that chain propagation reactions (IIIa) and (V) are the initial steps of the development of a chain process in the gas phase. According to current concepts [3, 9, 59], the methyl hydroperoxide species CH_3O_2H is responsible for chain branching in the oxidation of methane at medium pressures. The formation of this species is described by step (VI) (Table 4) in the oxidation reaction scheme [9]. The activation energy $E_a = 179.9$ kJ/mol of reaction (VII) of the decomposition of the above species into $CH_3O^\bullet$ and $HO^\bullet$ radicals is much higher than the values of 61 and 120 kJ/mol obtained in this work for the

apparent activation energy of formaldehyde formation in the gas phase. Reaction (VIII) in the scheme [9] is also characterized by a higher activation energy (E_a = 140 kJ/mol), and it occurs only in the collisions of $CH_3O^\bullet$ with other particles [59]. Under the conditions of our experiments, the participation of the above reactions in formaldehyde formation seems unlikely.

The temperature dependence of the steady-state rate of formaldehyde formation obtained in this work and published data [59] on the activation energies of the elementary steps of methane oxidation allowed us to hypothesize that reaction (IIIb) (Table 4) is responsible for process branching in our experiments. This reaction implies two directions in the development of the process depending on the subsequent transformations of the $CH_3O^\bullet$ radical and the oxygen atom. The transformations of the $CH_3O^\bullet$ radical can be described by reactions (IX) and (X) of the scheme [9], although the $HO_2^\bullet$ radical, which is formed in reaction (IX), is considered inactive [3] and we failed to detect hydrogen peroxide, which is formed in reaction (X), in the reaction products. Karmilova et al. [60], who described experiments on methane oxidation, experimentally detected H_2O_2 only in a quartz reactor treated with HF at temperatures of no higher than 500°C and at long contact times. It is likely that, at high temperatures, H_2O_2 is rapidly converted into more stable compounds such as H_2O [3]. At the same time, as the temperature and starting mixture feed rate were increased, we experimentally observed a change of the process to unstable conditions. With consideration for this fact, we can assume a higher probability of the latter direction in the development of the process through branching step (IIIc) (Table 4), in which $C^\bullet H_3$ and $HO^\bullet$ active radicals are formed.

Using the above hypothetical reaction scheme of methane oxidation to formaldehyde as applied to the conditions of our experiments, we discuss the results of studying the temperature dependence of the rate of formaldehyde formation (Table 3) and the effect of silica packing materials on the kinetics of the process (Table 2).

The appearance of the catalytic properties of a silica surface in the reaction of methane oxidation at high temperatures, namely, the ability of SiO_2 to activate methane with the formation of formaldehyde and/or $C^\bullet H_3$ free radicals at temperatures above 600°C, is an important result. These free radicals initiate rapid chain reactions of formaldehyde formation in the gas phase. The residence time (t_r) of a reaction mixture in the reaction volume is the most important process parameter. At short residence times (no longer than 0.01 s) and the complete removal of formaldehyde from the reaction zone, the oxidation occurred by a branched chain radical mechanism with almost 100% selectivity for formaldehyde. The reaction scheme of this mechanism hypothetically includes a number of free-radical reactions (Table 4): chain propagation, (IIIa), (V), (IX), and (X); chain branching, (IIIb) and (IIIc); radical decay, (IIId) and, likely, (IIIe). In this case, the length of chains and the probability of chain branching depend on the feed rate of the initial gas mixture (v°). At high values of v° and $T \geq 750$°C, the occurrence of the process can change to nonlinear conditions with critical phenomena.

As the residence time of the mixture in the reaction volume was increased, the degree of branching of the process increased as a result of reactions (XI)–(XVI) of the decomposition and oxidation of the primary molecular product formaldehyde. This resulted in a decrease in Y and S_{CH_2O} and the appearance of carbon oxides in the reaction products (Table 2). Karmilova et al. [61] found that the rate of homogeneous gas-phase methane oxidation increased by a factor of tens on the addition of a small amount (0.1–0.2%) of CH_2O to a methane–oxygen mixture. Therefore, the greatest degree of the chain process with a large chain length and chain branching was observed in an empty reaction volume even at t_r of about 0.02 s. In this case, the smallest changes in reaction conditions can cause a dramatic change in the kinetics of the process, for example, the appearance of self-oscillations accompanied by cold light. Detailed studies of nonlinear phenomena in the oxidation of methane to formaldehyde are beyond the scope of this paper, although such studies can be of considerable practical importance.

The contact surface area and the sizes and shapes of voids that constitute the free reaction volume are important parameters affecting the distribution of reaction products in the homogeneous–heterogeneous oxidation of methane to formaldehyde. The effect of these parameters on the kinetics of the process can be due to the reactions of free radicals, for example, $HO^\bullet$, with the surface, which lead to the loss of a free valence and chain termination. The probability of heterogeneous reactions of free radical recombination increases on narrowing the reaction space [52]. According to published data [3], the sticking coefficients of $C^\bullet H_3$ radicals to oxide surfaces such as ZnO and CeO_2 are very low (about 10^{-5}–10^{-3}). Therefore, according to Arutyunov and Krylov [3], the incident $C^\bullet H_3$ radical can be repeatedly reflected from the surface before reacting with it. Based on indirect data, Sun et al. [14] assumed that the methyl radicals that escaped into the gas phase were not adsorbed on the surface of SiO_2 once again. Our data (Table 2, entry 8) indicate that the reaction of formaldehyde formation in the gas phase was not suppressed even on increasing many times the surface area of silica packing material and decreasing the size of voids that constitute the free reaction volume. In this case, a decrease in the yield of and selectivity for formaldehyde accompanied by an increase in selectivities for carbon oxides was observed. This may be explained

Table 5. Comparative activity of catalysts for methane oxidation to formaldehyde

Entry	Catalyst	T, °C	v°, l/h	$v^\circ_{CH_4}$, l/h	v, l/h	n	w, mmol/h	Y, %	X, %	m_{CH_4}	m_{CO}	m_{CO_2}	S_{CH_2O}, %	S_{CO}, %	S_{CO_2}, %
1	IK-1-4	750	1.02	0.493	0.404	1700	7.7	35.0	66.8	0.405	0.017	0.327	52.4	2.2	40.2
2	AShNTs	750	1.00	0.480	0.359	1900	7.7	36.0	70.6	0.395	0.145	0.232	51.0	15.4	24.6
3	K1 (0.02% V)	750	1.02	0.507	0.385	1800	7.0	31.0	63.3	0.485	0.140	0.240	49.0	16.8	29.0
4	K2 (0.66% V)	750	1.01	0.503	0.470	1500	2.8	12.5	56.3	0.470	0.022	0.413	22.2	3.7	69.0
5	K3 (0.03% Pt)	750	0.962	0.460	0.471	1500	5.6	27.3	50.7	0.480	0.002	0.241	53.8	0.3	48.5
6	K3 (0.03% Pt)	680	0.961	0.460	0.851	800	2.1	10.2	10.7	0.482	–	0.005	95.5	–	8.6
7	K3 (0.03% Pt)	620	0.961	0.462	0.927	750	0.89	4.3	4.3	–	–	–	100.0	–	–
	Comparison with data in Table 2														
2	Tubes	750	0.99	0.501	0.308	2300	11.2	50.0	68.2	0.493	0.120	0.167	73.3	11.0	15.0
3	Quartz (2–3 mm)	750	1.01	0.500	0.47	1500	8.6	38.4	54.1	0.433	0.073	0.106	71.0	13.0	18.0
7	SSB-20 (threads)	750	1.03	0.517	0.472	1500	7.0	30.4	54.1	0.425	0.088	0.19	56.2	14.8	31.9

by the fact that a portion of $C^\bullet H_3$ and $HO^\bullet$ radicals was consumed in reactions (XI) and (XIV), which are energetically most favorable [59], to redistribute products in favor of CO and CO_2 as the reaction space was narrowed.

The question reasonably arises of whether other catalytic systems, such as typical oxidation catalysts, exhibit advantages over silicas. With the use of the same experimental procedure as in the case of silica samples, we performed experiments with well-known commercial IK-1-4 and AShNTs-3 catalysts, as well as activated fiberglass catalysts K_1, K_2, and K_3. We found that, even at a high circulation ratio and times $t_r \approx$ 0.01 s, the replacement of quartz tubes in the reaction volume (15 cm^3) with the above catalysts resulted in a dramatic decrease in the yield of and selectivity for formaldehyde up to the complete absence of formaldehyde from the reaction products and in the occurrence of a deep oxidation process. Various variations in the reaction temperature, grain size, and catalyst amount, as well as various catalyst bed (or beds) arrangements in the reaction volume either without or with the addition of a quartz glass packing material, did not allow us to obtain results better than those obtained on pure silica.

As an example, Table 5 summarizes the best results of the comparative tests of some of the above catalysts under conditions (test procedure and the filing of the reaction volume) comparable to the conditions of testing silica samples. In particular, small catalysts amounts (0.5 g) as granules of size 2–3 mm (IK-1-4 and AShNTs-3) or filaments (K_1, K_2, and K_3) were arranged on a quartz grate at the bottom of the reaction volume. The catalysts occupied no more than 1 cm^3 of the reaction volume. The remaining part of the volume was filled to the top with quartz tubes. The circulation flow rate was 700 l/h, and the residence time on the addition of catalysts was about 0.01–0.015 s. The sizes of voids between IK-1-4 and AShNTs-3 catalyst granules (2–3 mm) were the same as those in experiment no. 3 (Table 2). However, with consideration for the pore structure of a catalyst, the total available contact surface area in the catalyst bed increased to ~30000 cm^2. In the case of catalysts K_1, K_2, and K_3, the sizes of voids between filaments and the contact surface areas in filament layers were approximately consistent with the conditions of experiment no. 7 (Table 2).

To compare the results obtained in the tests of catalysts (Table 5) and silica samples, entries 2, 3, and 7 from Table 2 were chosen under approximately identical conditions of filing the reaction volume.

A comparison between data in Tables 2 and 5 indicates that the activity of catalysts used in the partial oxidation of methane under the conditions chosen was no higher than the activity of quartz glass and silica fiber samples. However, the presence of active commercial oxidation catalysts dramatically affected the distribution of reaction products. As can be seen in Table 5, the presence of these catalysts in the reaction volume resulted in a decrease in the yield of and the selectivity for formaldehyde and in an increase (particularly, in the case of catalyst nos. 1, 4, and 5) in the process selectivity for CO_2. The apparent activation energy of formaldehyde formation in the oxidation of methane in the presence of a 0.03% Pt/glass cloth catalyst was calculated from experimental data (Table 5, entries 5–7). The resulting value of 110 kJ/mol is close to an activation energy of 120 kJ/mol for the formation of formaldehyde in a heterogeneous–homogeneous reaction of methane oxidation on silica at $t_r = 0.01$ s and $v^\circ = 0.9$ l/h.

CONCLUSIONS

In this work, we found that the use of an improved FCR with reaction mixture quenching for studying the direct oxidation of methane to formaldehyde significantly improved the reliability of experimental data on the kinetics and mechanism of the process under discussion.

In particular, the study performed allows us to make the following conclusions:

(1) At high temperatures, starting at 600°C, the oxidation of methane to formaldehyde in the presence of a surface containing SiO_2 (quartz reactor walls, the surface of a silica packing material, or the surface of SiO_2 as a catalyst constituent) occurs by a heterogeneous–homogeneous mechanism with process initiation (the formation of free radicals) on a solid surface and chain propagation in the volume of the gas phase. In this case, SiO_2 can activate methane with the release of $C^{\bullet}H_3$ radicals into the volume; these radicals initiate rapid free-radical reactions of formaldehyde formation in the gas phase. However, it is likely that, as assumed previously, the recombination of $C^{\bullet}H_3$ free radicals on the surface of SiO_2 does not occur.

(2) Unlike purely homogeneous gas-phase oxidation, the rate of the heterogeneous–homogeneous methane oxidation to formaldehyde can be controlled, for example, using a silica packing material by changing the size and shape of the free reaction volume, as well as the contact surface area and the residence time of a mixture in the reaction volume.

(3) The heterogeneous–homogeneous process of methane oxidation under optimum conditions allows one to increase the integral yield of formaldehyde in a flow circulation system to 100%. This is achieved at short residence times of a mixture in the reactor and by process transfer to a homogeneous gas phase, where methyl radicals are generated at a high rate in radical-chain reactions. In this case, it is likely that the rate of formaldehyde formation is controlled by reaction (IIIa) or (IIIb) involving the interaction of oxygen molecules with $C^{\bullet}H_3$ radicals in the volume. The activation energies of these elementary reactions are much lower than the activation energy of an elementary heterogeneous reaction of formaldehyde formation on the surface of SiO_2.

(4) The introduction of typical oxidation catalysts containing, for example, Pt or V_2O_5 as an active component into the reaction volume results in a decrease in the integral yield of and selectivity for formaldehyde, as compared with those on pure SiO_2 samples. This is due to the fact that the activity of the above oxidation catalysts in the secondary reactions of formaldehyde conversion (decomposition and oxidation) into the thermodynamically most stable products (carbon oxides) is much higher than that of SiO_2. Thus, it is likely that, among the well-known catalytic systems for direct methane oxidation, silicas are the most efficient catalysts for the heterogeneous–homogeneous oxidation of methane to formaldehyde. In turn, the heterogeneous–homogeneous oxidation of methane is a more efficient process for formaldehyde production than heterogeneous oxidation.

REFERENCES

1. Brown, M.J. and Parkins, N.D., *Catal. Today*, 1991, vol. 8, no. 3, p. 305.
2. Parkins, N.D., Warburton, C.I., and Wilson, J.D., *Catal. Today*, 1993, vol. 18, no. 4, p. 385.
3. Arutyunov, V.S. and Krylov, O.V., *Okislitel'nye prevrashcheniya metana* (Methane Oxidations), Moscow: Nauka, 1998.
4. Sexton, A.W., Kartheuser, B., Batiot, C., Zanthoff, H.W., and Hodnett, B.K., *Catal. Today,* 1998, vol. 40, p. 245.
5. Kastanas, G., Tsigdinos, G., and Schwank, J., *Spring National AIChe Meeting*, Houston, Tex., 1989, paper 52d.
6. Yamaguchi, T., Echigoya, E., Sai, S., and Sueyoshi, M., *Appl. Catal.*, 1986, vol. 26, p. 410.
7. Otsuka, K, Komatsu, T, Jinno, K, Uragami, Y, and Morikawa, A, in *Proc. 9th Int. Congr. on Catalysis*, Philips, M.J. and Ternan, M., Eds., Ottawa, 1988, vol. 2, p. 915.
8. Amir-Ebrahimi, V. and Rooney, J.J., *J. Mol. Catal.*, 1989, vol. 50, p. L17.
9. Baldwin, T.R., Burch, R., Squire, G.D., and Tsang, S.C., *Appl. Catal.*, 1991, vol. 74, p. 137.
10. Spencer, N.D., *J. Catal.*, 1988, vol. 109, no. 1, p. 187.
11. Parmaliana, A., Sokolovskii, V., Miceli, D., Arena, F., and Giordano, N., *J. Catal.,* 1994, vol. 148, p. 514.
12. Kastanas, G., Tsigdinos, G., and Schwank, J., *Appl. Catal.*, 1988, vol. 44, p. 33.
13. Parmaliana, A., Frusteri, F., Miceli, D., Mezzapica, A., Scurrell, M.S., and Giordano, N., *Appl. Catal.*, 1991, vol. 78. p. L7.
14. Sun, Q., Herman, R., and Klier, K., *Catal. Lett.*, 1992, vol. 16, p. 251.
15. Brei, V.V., Gun'ko, V.M., Khavryuchenko, V.D., and Chuiko, A.A., *Kinet. Katal.*, 1990, vol. 31, no. 5, p. 1164.
16. Sun, Q., Cosimo, J., Herman, R., Hermann, R.G., Klier, K., and Bhasin, M.M., *Catal. Lett.*, 1992, vol. 15, p. 371.
17. Parmaliana, A., Arena, F., Frusteri, F., Martinez-Arias, A., Granados, M.L., and Fierro, J.L.G., *Appl. Catal., A*, 2002, vol. 202, p. 163.
18. Arena, F. and Parmaliana, A., *Acc. Chem. Res.*, 2003, vol. 36, no. 12, p. 867.
19. Stadnik, P.M. and Gomonai, V.I., *Ukr. Khim. Zh.*, 1963, vol. 29, no. 4, p. 1052.
20. Stadnik, P.M. and Gomonai, V.I., *Kinet. Katal.*, 1963, vol. 4, no. 3, p. 348.

21. Margolis, L.Ya., Nersesyan, L.A., and Nalbandyan, A.B., in *Trudy Vsesoyuznoi konferentsii po mekhanizmu katalitiicheskikh reaktsii* (Proc. USSR Conf. on Mechanisms of Catalytic Reactions), Moscow, 1974, prepr. 75.

22. Nersesyan, L.A., Vardanyan, I.A., Kegeyan, E.M., Margolis, L.Ya., and Nalbandyan, A.B., *Dokl. Akad. Nauk SSSR*, 1973, vol. 220, no. 3, p. 606.

23. Gomonai, V.I., *Kataliz i Katalizatory*, 1989, vol. 26, p. 52.

24. Banares, M.A., Cardoso, J.H., Hutchings, G.J., Bueno, J.M.C., and Fierro, J.L.G., *Catal. Lett.*, 1988, vol. 56, p. 149.

25. Yu, L., Yuan, S., Wu, Z., Wan, J., Gang, M., Pan, G., and Chen, Y., *Appl. Catal., A*, 1998, vol. 171, p. L171.

26. Spencer, N. and Pereira, D., *J. Catal.*, 1989, vol. 116, p. 399.

27. Otsuka, K. and Wang, Y., *Appl. Catal., A*, 2001, vol. 222, p. 145.

28. McCormick, R.L., Al-Sahali, M.B., and Alptekin, G.O., *Appl. Catal., A*, 2002, vol. 226, p. 129.

29. Kartheuser, B., Hodnett, B.K., Zanthoffard, H., and Baerns, M., *Catal. Lett.*, 1993, vol. 21, p. 209.

30. Bobrov, N.N., *Kursy povysheniya kvalifikatsii po katalizatoram i kataliticheskim protsessam* (Advanced Training Course on Catalysts and Catalytic Processes), Novosibirsk: Inst. Kataliza, 2002, p. 146.

31. Bobrov, N.N., Bobrova, I.I., and Sobyanin, V.A., *Kinet. Katal.*, 1993, vol. 34, no. 4, p. 686.

32. Sinev, M.Yu., *J. Catal.*, 2003, vol. 216, p. 468.

33. Berndt, H., Martin, A., Bruckner, A., Schreier, E., Muller, D., Kosslick, H., Wolf, G.-U., and Lucke, B., *J. Catal.*, 2000, vol. 191, p. 384.

34. Bobrov, N.N. and Parmon, V.N., in *Principles and Methods for Accelerated Catalyst Design and Testing*, NATO Science Series II: Mathematics, Physics and Chemistry, vol. 69, Dordrecht: Kluwer, 2002, p. 197.

35. Bobrova, I.I., Chesnokov, V.V., Bobrov, N.N., Zaikovskii, V.I., and Parmon, V.N., *Kinet. Katal.*, 2000, vol. 41, no. 1, p. 25 [*Kinet. Catal.* (Engl. Transl.), vol. 41, no. 1, p. 19].

36. Bobrova, I.I., Bobrov, N.N., Chesnokov, V.V., and Parmon, V.N., *Kinet. Katal.*, 2001, vol. 42, no. 6, p. 882 [*Kinet. Catal.* (Engl. Transl.), vol. 42, no. 6, p. 805].

37. Gomonai, V.I., *Doctoral (Chem.) Dissertation*, Uzhgorod: Uzhgorod State Univ., 1990.

38. Mukhlenov, I.P., Vilenskii, A.R., Zuev, I.A., Prokopenko, A.N., Arnautova, G.M., and Emel'yanova, I.N., *Geterogennye kataliticheskie protsessy* (Heterogeneous Catalytic Processes), Leningrad: Leningrad. Tekhnol. Inst. im. Lensoveta, 1986, p. 101.

39. Temkin, M.I., Kiperman, S.L., and Luk'yanova, L.I., *Dokl. Akad. Nauk SSSR*, 1950, vol. 74, p. 763.

40. USSR Inventor's Certificate no. 958407, *Byull. Izobret.*, 1982, no. 34.

41. Bafas, I.C., Constantinou, I.E., and Vayenas, C.G., *Chem. Eng. Sci.*, 2001, vol. 82, p. 109.

42. RF Patent 2037651, 1995.

43. RF Patent 2085269, 1997.

44. Bobrov, N.N., Leonov, A.S., Belov, A.N., Demidov, M.B., Titov, V.P., Vanin, E.A., and Lipitanov, P.P., *Katal. Prom–sti.*, 2005, no. 2, p. 50.

45. Winkelman, J.G.M., Voorwinde, O.K., Ottens, M., Beenacker, A.A.C.M., and Janssen, L.P.B., *Chem. Eng. Sci.*, 2002, vol. 57, p. 4067.

46. Walker, J.F., *Formaldehyde*, New York: Reinhold, 1964, p. 489.

47. Simonova, L.G., Barelko, V.V., Lapina, O.B., Paukshtis, E.A., Terskikh, V.V., Zaikovskii, V.I., and Bal'zhinimaev, B.S., *Kinet. Katal.*, 2001, vol. 42, no. 5, p. 762 [*Kinet. Catal.* (Engl. Transl.), vol. 42, no. 5, p. 693].

48. Vandooren, J. and van Tiggelen, P.J., *Symp. (Int.) Combust.*, 1981, vol. 18, p. 473.

49. Miyauchi, T., Mori, Y., and Imamura, A., *Symp. (Int.) Combust.*, 1977, vol. 16, p. 1073.

50. Baulch, D.L., Cobos, C.J., Cox, R.A., et al., *J. Phys. Chem. Ref. Data*, 1992, vol. 21, p. 411.

51. Tsang, W. and Hampson, R.F., *J. Phys. Chem. Ref. Data*, 1986, vol. 15, p. 1087.

52. Semenov, N.N., *Tsepnye reaktsii* (Chain Reactions), Moscow: Nauka, 1986.

53. Askey, P.J., *J. Am. Chem. Soc.*, 1930, vol. 52, p. 2753.

54. Evlanov, S.F. and Lavrov, N.V., *Nauchnye osnovy kataliticheskoi konversii uglevodorodov* (Scientific Foundations of the Catalytic Conversion of Hydrocarbons), Kiev: Naukova Dumka, 1977, p. 210.

55. Matveev, A.V., *Extended Abstract of Cand. Sci. (Chem.) Dissertation*, Novosibirsk: Inst. of Catalysis, 2004.

56. Bazhin, N.M., Ivanchenko, V.A., and Parmon, V.N., *Termodinamika dlya khimikov* (Thermodynamics for Chemists), Moscow: KolosS, 2004.

57. Parmon, V.N., *Lektsii po termodinamike neravnovesnykh protsessov dlya khimikov* (Lectures on Nonequilibrium Thermodynamics for Chemists), Novosibirsk: Novosibirsk. Gos. Univ., 2005.

58. Karmilova, L.V., Enikolopyan, N.S., Nalbandyan, A.B., and Semenov, N.N., *Zh. Fiz. Khim.*, 1960, vol. 34, no. 6, p. 1176.

59. Vedeneev, V.I., Krylov, O.V., Arutyunov, V.S., Basevich, V.Ya., Goldenberg, M.Ya., and Teitelboim, M.A., *Appl. Catal., A*, 1995, vol. 127, p. 51.

60. Karmilova, L.V., Enikolopyan, N.S., and Nalbandyan, A.B., *Zh. Fiz. Khim.*, 1960, vol. 34, no. 5, p. 990.

61. Karmilova, L.V., Enikolopyan, N.S., and Nalbandyan, A.B., *Zh. Fiz. Khim.*, 1957, vol. 31, no. 4, p. 851.