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The role of pressure in partial oxidation of methane

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Analysis of experimental data and results of kinetic simulation throw light on the reasons for which the pressure exerts influence on the partial oxidation of methane to methanol. Among the most important factors are a crucial transition of the reaction to the steady-state chain-branched regime, an increase in the role of nonlinear gas-phase reactions, and a change in the relative contribution of heterogeneous transformations to the overall process.

Key words: methane, methanol, formaldehyde, partial oxidation.

The direct oxidative conversion of methane to methanol, which can approximately be described by the overall equation

$$2\,CH_4 + 2\,O_2 \begin{cases} \rightarrow 0.9\,MeOH + 0.1\,(CH_2O + H_2) \\ \rightarrow 0.9\,(CO + 2\,H_2O) + 0.1\,(CO_2 + H_2 + H_2O), \end{cases}$$

is one of the promising methods for involvement of huge resources of the natural gas in chemical processing.[1,2] Although the kinetics of direct homogeneous methane oxidation at high pressures is under intense study, the role of the pressure in this complicated chain-branched process remains unclear. Analysis of the available data suggests that the effect of pressure on the yield of methanol depends on structural features of laboratory reactors, including their size and material of the surface. Investigations in this direction are important for understanding of the kinetics of the process and, moreover, challenges for its practical realization, because in the partial oxidation of the natural gas the working pressure has a strong effect on the economical parameters. In this work, we examined the role of the pressure in the direct oxidation of methane to methanol (DOMM) on the basis of published experimental data and results of kinetic simulation.

Experimental data on the effect of pressure on the yield of methanol

Although methanol forms at an atmospheric pressure as well, already the first studies[1,2] on DOMM have shown that a high total pressure (~50—100 atm), along with the high $CH_4 : O_2$ ratio, are key conditions to achieve a significant selectivity toward methanol. For example, in a quartz reactor at 450 °C and a contact time of 1.5 min the selectivity of methanol formation (S_{MeOH}) in a CH_4—O_2 (2 : 1) mixture reaches 41% but decreases with an increase in the contact time.[3]

Under static conditions at the contact time to several tens of minutes, the selectivity of methanol formation increases[4,5] steadily with the pressure increase from 10 to 106 atm. However, the highest selectivity (51%) was achieved[6] under jet conditions at a pressure of only 50 atm and a contact time of 5 s.

Analysis of the published data suggests that the influence of the pressure on methanol formation depends on the material and sizes of the reactor used and the time of the reaction (τ_r), *i.e.*, the time necessary for the complete conversion of oxygen under the experimental conditions. Under jet conditions, the lowest yield of methanol at the pressures from 50 to 300 atm was observed in a copper reactor with a small diameter (~10 mm)[7] (Fig. 1). Under the same pressures, the yield of methanol is much higher in stainless steel reactors with a greater diameter (25 mm).[8,9] At the approximately same diameter of stainless steel reactors, the higher yield of methanol was achieved in experiments[8] in which τ_r was ~1 s compared to the experiments[9] in which τ_r was tens of seconds or minutes. As can be seen from the comparison of the published data (see Fig. 1), the material of the surface (stainless steel and quartz[10]; stainless steel, quartz, and Pyrex[11]) strongly affects the character of the plots of the yield of methanol and S_{MeOH}[11] *vs.* pressure.[10] The influence of the material is low at high pressures, but it is manifested rather clear at a reduced pressure. For example, in stainless steel reactors the yield of methanol decreases rapidly with a decrease in the pressure, while in quartz reactors the dependence of the yield of MeOH on the pressure is much weaker. As has been shown,[11] the different behavior of these materials is not related to the different decomposi-

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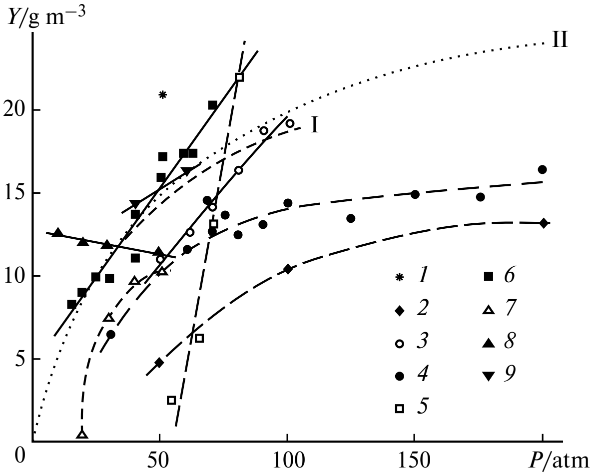

Fig. 1. Dependence of the yield of methanol (Y) on the total pressure (P) in the system in partial methane oxidation in entries *1—9*. I is the calculation using the model[1,2] under the conditions $[O_2]$ = 3.5%, diameter of the reactor 10 mm, T = 480 °C; II is the calculation by the formula $[MeOH] = [MeOH]_\infty/(1 + P_{0.5}/P)$.

Entry	$[O_2]$ (%)	Diameter of reaction/mm	Material of reactor	T/°C	τ_r/s	Refs.
1	3	3	Steel	430	5	4
2	3	~10	Copper	475	1.8	7
3	2.8	25	Steel (st.)*	410	1	8
4	2.7—2.9	25	Steel (st.)*	410	30—40**	9
5	3.6	10	Steel (st.)*	500	3	10
6	3.6	7	Quartz	500	~3	10
7	2.5	4	Steel (st.)*	450	~100	11
8	2.5	4	Quartz	450	~100	11
9	2.7	20	Al_2O_3	430—450	~1	12

* Stainless steel.

** Figures at the same pressures were averaged.

tion rates of methanol that has been formed on the corresponding surfaces and are due to the influence of the surface on the kinetics of the process at the step of methane oxidation. A weak effect of the pressure on the reaction kinetics was also observed in Al_2O_3 (alsint) reactors.[12]

Although the maximum yield of methanol in quartz and stainless steel reactors is almost the same at high pressures, a higher initial oxygen concentration is needed to achieve the maximum yield on the quartz surface.[10]

The formation of methanol as an intermediate product in the oxidation of rich methane—oxygen mixtures at low pressures was reported in several works.[13—16] The intermediate S_{MeOH} values even reached 20% in the oxidation at an atmospheric pressure,[14] although the final selectivity at the complete oxygen conversion did not exceed 5%. At the initial oxidation stages, a relatively high S_{MeOH} value (higher than 30%) was observed at pressures of 1.5—3 atm. However, it decreased[15] to 10% with an increase in the conversion of methane. Under static conditions, for the oxidation of rich CH_4—O_2 (16 : 1) mixtures in a quartz reactor at 450 °C and a pressure of only 350 Torr, the S_{MeOH} value reached 10% with respect to the consumed oxygen.[16]

The role of pressure in the partial oxidation of methane

Regime of the steady-state chain-branched reaction. In the general case, methane oxidation at high pressures occurs *via* the chain-branched mechanism.[1,2] The kinetic simulation[17] performed for a CH_4—O_2 (9 : 1) mixture for temperatures of 600—750 K and pressures of 1—100 atm indicated that the reaction time τ_r shows a stepwise decrease by 3—4 orders of magnitude with a slight pressure change in the range of several atm (Fig. 2). Such a decrease can be induced only by a change in the mechanism of the process. A sharp increase in the reaction rate can be explained by its transition from the regime of a chain process, which rate is controlled by the strongly endothermic slow step of homogeneous chain initiation, to the regime of a steady-state chain-branched process.[1,2] In this regime, the oxidation rate is determined by chain branching reactions, whose rate is several orders higher than the rate of homogeneous radical initiation. However, the further increase in the concentration of radicals is restricted by their square recombination.

The results of calculations[17] explain the failure of numerous attempts to enhance the efficiency of the direct oxidation of methane by the use of heterogeneous catalysts. Although in the presence of the catalyst the rate of radical generation is higher than that of their thermal initiation, at sufficiently high pressures in the regime of the steady-state chain-branched reaction the intensity of radical generation on the catalyst cannot compete with the intensity of their generation in the chain branching stages. Therefore, heterogeneous catalysts, homogeneous

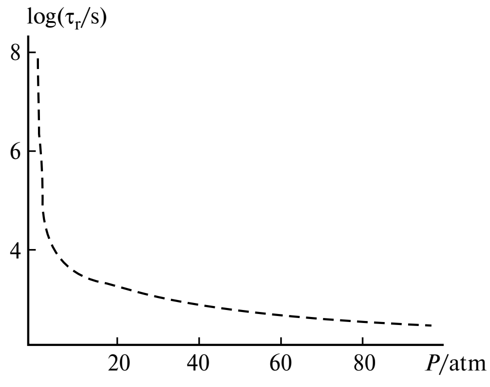

Fig. 2. Semilogarithmic dependence of the time of partial methane oxidation (τ_r) on the total pressure in the system. The calculation[17] was for the CH_4—O_2 (9 : 1) system at 650 K.

promoters, and other methods of initiation have no significant influence on the DOMM process. The efficient effect of the catalyst on the process can be expected if the rate of catalytic radical generation is comparable with the rate of their generation in homogeneous branching reactions, whose rates, according to the kinetic calculations,[17] exceed the rate of homogeneous thermal initiation by at least 10^4 times. The existence of such catalysts has not yet been reported.

The pressure of the crucial transition depends on other experimental parameters and equals several atm, and the calculated plot of the reaction time *vs.* pressure (see Fig. 2) corresponds to the experimental data. Thus, the pressure value determines the transition of the system from the regime of slow chain reaction to the regime of fast steady-state chain-branched reaction.

Influence of the pressure on the rate of the steady-state chain-branched reaction. The results of kinetic simulation show (see Fig. 2) that after the jump-like transition of the system to the regime of the steady-state chain-branched reaction, the pressure increase is accompanied by a steady increase in the rate of the process. The pressure increase accelerates the oxidation of methane decreasing the time and/or temperature of the reaction. According to the experimental data,[18] the dependence of the delay time of self-ignition of a methane—air (8.8 : 1.2) mixture on the pressure in the interval from 60 to 113 atm is described by the expression $\tau_r \sim P^{-1.4}$, which is in good accord with the results of kinetic simulation. For example, the close expression $\tau_r \sim P^{-1.2}$ can be obtained from the plot presented in Fig. 2 for a methane—oxygen (9 : 1) mixture in the pressure interval from 20 to 100 atm.

An increase in the pressure at a constant residence time of the reaction mixture in the reactor decreases the temperature of initial oxidation and the temperature of complete oxygen conversion. Figure 3 presents the data[10,11,19] obtained in jet reactors close in size (4—7 mm in diameter). The data show that the pressure increase from 1 to 80 atm decreases the temperature of initial conversion of oxygen from >650 to 375 °C, whereas the temperature of its complete conversion decreases from >700 to ~440 °C. At low pressures a promoter additive has a similar effect on the process. For example, under conditions described (5 atm),[19] the introduction of 0.5% nitrogen oxide decreases the reaction temperature by ~100 °C. However, the promotion effect from the addition of nitrogen oxide decreases with an increase in the pressure (as well as with an increase in the NO concentration), and pressures <10 atm are optimum for promotion.

Influence of the pressure on the yield of methanol. The effect of pressure on the gas-phase process can be manifested, in particular, in the dependence of the rate constants of elementary reactions on this parameter. However, for the partial oxidation of methane at the pressures >10 atm almost all rate constants are in the region of "infinitely high pressure," *i.e.*, they change insignificantly with the further pressure increase.

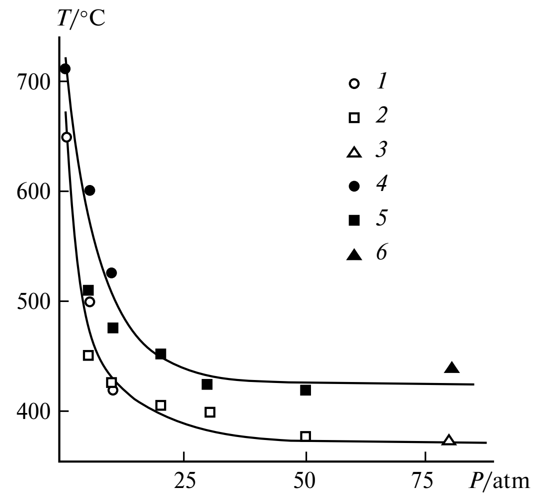

Fig. 3. Dependence of the temperature of initial conversion (*1—3*) and complete conversion of oxygen (*4—6*) on the total pressure in the system: *1*, *4*, by Ref. 19; *2* and *5*, by Ref. 11; and *3*, *6*, by Ref. 10.

A hypothesis was advanced[20] about the possible manifestation of the "cage effect" during methane oxidation in the region of pressures higher than 100 atm. However, experiments in static reactors under pressures of several thousands of atm[21,22] did not confirm this assumption.

The kinetic analysis shows[1,2] that an increase in the partial pressure of reactants should result in an increase in the overall rate of oxidation and also in an enhancement of the role of nonlinear radical gas-phase reactions. This can result in an increase in the selectivity of methanol formation.

The most reliable published experimental data on the dependence of the yield of methanol on the pressure obtained at the oxygen conversions close to 100%, are presented in Fig. 1. All experiments were carried out under relatively similar conditions, optimum for the achievement of the high yield of methanol. The yield of methanol Y_{MeOH} was used as a measure because this parameter can most reliably be measured in experiment. The selectivity of methanol formation at a low conversion of methane is usually determined with high errors. Nevertheless, if authors did not present the yield of methanol, Y_{MeOH} was estimated from the selectivity of methanol formation. At a low concentration of oxygen characteristic of the DOMM process and its almost complete conversion, the conversion of methane almost coincides with the initial concentration of oxygen in the mixture.[2] The reason is that two main carbon-containing products, *viz.*, methanol and carbon monoxide, are formed in approximately equal amounts, in accord with the overall equation presented above. The yield of two next important carbon-containing products, *viz.*, formaldehyde and carbon dioxide, is ~10—15% of the yield of the corresponding main product. Their formation has almost no effect on the distribution of carbon, hydrogen, and oxygen between the liquid-phase and gas-phase reaction products. Therefore, the yield of methanol can be estimated using the expression

$$Y_{\mathrm{MeOH}} = QxS_{\mathrm{MeOH}},$$

where Q is the consumption of methane, x is its conversion equal to the initial concentration of oxygen, and S_{MeOH} is the selectivity to methanol formation.

The initial concentration of oxygen in experiments (see Fig. 1) varied from 2.5 to 3.6%. Exactly speaking, the conversion of methane and, hence, the yield of methanol depend on the initial concentration of oxygen in the mixture and at low concentrations of O_2 they are virtually equal to $[O_2]$ (all experimental data are presented in Fig. 1 in the original form, without reducing to the same conversion). This increases the divergence of the results no more than by 30%. In independent studies, the reaction temperature was varied depending on other conditions. However, as a whole, it was in a sufficiently narrow interval (410—500 °C). The reaction time ranged from several unities to several tens of seconds. Reactors with the surface covered by stainless steel, copper, quartz, Pyrex, or Al_2O_3 (alsint) were 4—25 mm in diameter.

Taking into account slight differences in conversion, the data presented agree well with each other and results of the kinetic simulation of the process. Taking into account the difference in the initial oxygen concentrations, we have to accept that the results obtained at pressures higher than 70 atm[8,10] almost coincide, despite the different diameters of the reactors (25 and 10 mm), different characters of flow (turbulent and laminar, respectively), and a lack of the perfect coincidence of τ_r. The lower yield of methanol in Ref. 9 can be explained by a much longer residence time of the gas mixture in the reactor.

In reactors with a small diameter, the material covering surface affects the yield of methanol especially strongly, although the slight increase in the selectivity of methanol formation on the quartz surface[11] with a decrease in the pressure can be explained by inaccuracies of the experiment. Alumina (alsint) behaves like quartz.[12] The yield of methanol in reactors with the inert surface (quartz, Al_2O_3) increases almost linearly with an increase in the pressure to ~80 atm (except for the results in Ref. 11). Under comparable conditions, the plot of the yield *vs.* pressure is sharper on metallic surfaces.[10,11] The lowest yield of methanol is observed[7] on the copper surface up to 300 atm.

Despite difficulties of taking into account heterogeneous processes on the reactor surface, the calculations by the model[1,2] (see Fig. 1) allow the satisfactory description of experimental data on the yield of methanol and its pressure dependence.

Thus, at low pressures, long reaction times, and small diameters of the reactor, the material of the surface has a substantial effect on the yield of methanol. With reactors made of quartz, Pyrex, and alumina (alsint) at pressures to 80 atm the yield of methanol is higher than under similar conditions in reactors with the metallic surface. With reactors having a smaller diameter and a more active (metallic) surface, a sharper plot of the yield *vs.* pressure is observed.

The role of diffusion of reactants to the reactor surface. At pressures of 10—100 atm, the effect of pressure on the partial oxidation of methane can be best explained by a decrease in the rate of diffusion of components of the reaction mixture to the reactor surface. This is especially relevant to laboratory installations where reactors with small diameters and low rates of the gas flow are used. The influence of the pressure is determined by the structural features of the reactor (its diameter, surface material, and residence time of reactants in the reactor) and the partial pressure of inert diluents.

In all above-described experiments, the gas flow has a laminar character and, therefore, the rate constants of molecular diffusion can be used in calculations. Only the experiments on a pilot plant[8] were carried out under the turbulent flow conditions.

The time of diffusion of a substance to the surface in the laminar flow can easily be estimated using the known equation

$$\tau = d^2/\mu_1 D,$$

where d is the diameter of the reactor, μ_1 is the root of Bessel´s function, and D is the diffusion coefficient. The D coefficient is determined by the formula

$$D = D_0(1/P)(T/273)^{1.5},$$

where D_0 is the diffusion coefficient under standard conditions, P is the total pressure, and T is the reaction temperature (K). For the most experiments carried out on laboratory installations at ~50 atm, τ is several seconds and almost coincides with the residence time of the mixture in the reactor. Therefore, at pressures lower than 50 atm we can expect an appreciable interaction of the reaction mixture with the surface, which has a substantial effect on the yield of the oxidation products.

The influence of the surface on the course of the process was observed in several studies performed at pressures close to atmospheric. When methane is oxidized in reactors of copper, steel, aluminum, or Pyrex glass in a pressure interval of 1—4 atm at a contact time of 30—200 s, the material of the surface has a strong influence on the kinetics of the process.[23] In steel and especially copper reactors, the surface reaction predominates and carbon oxides and water are the main products. In glass reactors and, to a less extent, in alumina reactors methanol and formaldehyde are also formed. Based on these results, some authors concluded[23] that copper and iron oxides are active catalysts of the process.

When the pressure increases from 1 to 4 atm, the difference in the character of the reaction in metallic and glass reactors decreases.[24] The oxidation of light paraffins in steel or copper reactors, especially under an atmospheric pressure, affords smaller amounts of oxygenates (alcohols and aldehydes) than in glass reactors.[23]

At relatively low pressures in a metallic reactor or in the presence of a catalyst, the products of complete oxidation predominate, but at 40 atm the surface material has no substantial effect on methanol formation.[11] The selectivity decreases rapidly with a decrease in the pressure in a stainless steel reactor, and methanol was not detected at pressures below 20 atm. At the same time, in quartz and Pyrex reactors the selectivity to methanol remains almost unchanged (~40%) at pressures of 10—50 atm (see Fig. 1).

A negative effect on the formation of methanol was found when an additional metallic or quartz surface was introduced in the reactor.[25] A similar effect was observed for the influence of the oxide catalysts on methane oxidation (pressure 5 atm, methane : air ratio 1 : 5, temperature 625 °C).[26] This effect is attributed to the role of the surface in the heterogeneous radical decay.[27] The transition to more inert coatings and an increase in the reactor diameter at low pressures favor, as a rule, a higher selectivity to methanol. In reactors with the quartz[10,11] and Al_2O_3 (alsint) surfaces,[12] methanol forms with a high selectivity even at a relatively moderate pressure of 40 atm (see Fig. 1).

A decrease in the rate of diffusion of active species or oxygen to the reactor surface with the pressure increase is confirmed by the results of experiments[10] on the oxidation of methane diluted with nitrogen to the ratio $CH_4 : N_2 = 1 : 3$. Compared to experiments conducted with the same partial pressure of methane, higher yield of methanol was achieved in the case when the $CH_4 : O_2$ was the same but the overall pressure was higher.

The role of catalytic reactions on the surface. In addition to the decay of radicals leading the chain-branched process, catalytic reactions with the predominant formation of products of deep methane oxidation, *i.e.*, carbon oxides and water, can occur on the metallic surface of the reactors, especially on copper, iron, and nickel.

The supported platinum catalyst was experimentally shown[28] to accelerate the reaction between methane and oxygen and also to increase the fraction of the deep oxidation products, *i.e.*, it decreases the selectivity of gas-phase processes, including those producing methanol. Since the occurrence of the partial oxidation of methane to methanol needs the maintenance of the very low O_2 concentration, the gas-phase reaction of partial oxidation to oxygenates competes, in fact, with the surface catalytic reaction of deep oxidation for oxygen. At high pressures, the catalytic reaction rate is determined by the diffusion of the deficient reactant, oxygen, to the surface. The competition between the surface reactions and the gas-phase processes of partial oxidation for the deficient oxygen, which decreases with pressure, can likely be described by a simple expression

$$[\mathrm{MeOH}] = [\mathrm{MeOH}]_\infty/(1 + P_{0.5}/P),$$

where $[\mathrm{MeOH}]_\infty$ is the yield of methanol at an infinitely high pressure, P is the total pressure, and $P_{0.5}$ is the pressure at which the yield of methanol comprises a half of $[\mathrm{MeOH}]_\infty$. The corresponding curve plotted under the assumption that $[\mathrm{MeOH}]_\infty = 30$ g m^{-3} and $P_{0.5} = 50$ atm is presented in Fig. 1. As can be seen, this simple equation describes satisfactorily the run of the most part of experimental plots presented in Fig. 1.

Thus, there are several reasons which explain the influence of the pressure on the yield of methanol in the partial methane oxidation.

1. The crucial transition of the oxidation process to the regime of the steady-state chain-branched reaction occurs at pressures of several atm, and the reaction rate increases stepwise by several orders of magnitude.
2. At pressures below 10 atm, the rate constants of elementary mono- and trimolecular reactions increase to the values corresponding to the limit of "infinitely high pressure."
3. An increase in the overall pressure is accompanied by an increase in the partial pressure of reactants. Since the chain-branched oxidation process is nonlinear to a great extent, this can result in an increase in the overall rate and, moreover, an increase in the contribution of nonlinear gas-phase reactions yielding methanol.
4. A decrease in the diffusion rate with pressure decreases the contribution of heterogeneous processes, which afford mainly deep oxidation products.
5. An increase in the diameter of the reactor also decreases the contribution of heterogeneous processes, and due to this the pressure influence on the yield of methanol becomes less significant.
6. In reactors with a great diameter operated at pressures higher than 100 atm, a slight monotonic increase in the yield of methanol should be observed due to an increase in the rate of nonlinear gas-phase reactions yielding methanol.

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