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REVIEWS

Catalytic Partial Oxidation of Methane to Formaldehyde

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CATALYTIC SYSTEMS FOR METHANE OXIDATION TO FORMALDEHYDE

Formaldehyde is mostly manufactured from methanol, but, already in 1948, 20% of this compound was produced by direct oxidation of gaseous hydrocarbons. However, the industrial process for manufacture of formaldehyde by methane oxidation did not find use in the United States, but was implemented in Germany [1–3]. In this process, natural gas (98% CH_4) was oxidized with air in the presence of 0.08% nitric acid at 400–600°C. It is believed that the claimed yield of the target product, 35%, is 10-fold overstated [2], and the conversion of 10% is realistic. It is also known that, in oxidation of coke gas (74% CH_4) with ozonized oxygen at 110°C, the conversion of methane, including that to formaldehyde, may reach a value of 25% because of the admixtures present in methane (wt %): ethylene 3, nitrogen 12, carbon monoxide 11, and hydrogen 4.

It is highly difficult to perform incomplete oxidation of methane, because it has been shown that, at temperatures below 600°C, no noticeable oxidation of methane occurs, whereas formaldehyde starts to decompose at substantially lower temperatures [4]. It was considered that CH_2O is produced from CH_4 via the stage of CH_3OH formation (some researchers still adhere to this opinion [5]). It was noted in a review devoted to methane oxidation that, because of the occurrence of secondary processes, the residence duration of gases in the reaction zone should be short and, consequently, only a minor fraction of methane (presumably, up to 5%) can be converted to formaldehyde in a single run. This disagrees with the actual conversion of methane and relative amounts of its oxidation products.

In contrast to the aforesaid, another mechanism of methane conversion can be found in the literature [7]: $CH_4 \rightarrow CH_{4-x} \rightarrow CH_2O \rightarrow CO + CO_2$, in which the activity of a catalyst is determined by the rate of the first reaction, and its selectivity by the ratio between the rates of the second and third stages of the process. Detailed studies in this area have made it possible to verify the parallel-consecutive mechanism of the reaction of methane oxidation into formaldehyde and methanol [5]. However, analysis of schemes of the direction of substrate conversion is somewhat premature without any knowledge about the role of catalysts in this process.

Despite that the number of studies concerned with the catalytic oxidation of methane into formaldehyde is large, compared with oxidation into methanol, their overwhelming majority is devoted to analysis of the effect of MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts [8]. With these catalysts, the yield of formaldehyde does not exceed 3–4%, higher reported yields are not confirmed by other researchers. Interestingly, pure SiO_2 itself exhibits a noticeable catalytic activity [9].

To solve the problem of the theoretically possible yield, the thermodynamically possible degree of methane conversion has been calculated. For example, a comparison was made of the C–H bond energies in reactants and products formed in the reaction with the limiting selectivity were compared, as well as of the limiting yield of products of oxidative methane conversion in various processes with the equilibrium constant of deep dehydration of each of these products. In the first case, the authors of [10] believe that hydrocarbons are activated via rupture of the weakest C–H bond in a hydrocarbon; the loss of selectivity occurs in rupture of the weakest bond in the product. The

Main types of catalysts for methane oxidation to formaldehyde

Catalyst	*T*, °C	Conversion, %,	Selectivity, %	Yield, %	Reference
SiO_2	570	0.15	34	5.1	[12]
$A1_20_3$	650–670	17	11.6		[13]
MgO	750	2	60	1.2	[14]
MoO_3	600	1	85	0.85	[15]
$Sn_3(P0_4)_2$				2.0	[16]
81_2P_2O7/aluminosilicate + H_3PO_4	600	5.1	96	4.9	[17]
$8п_2P_2O_7$/aluminosilicate + H_3PO_4	600	9.0	96	8.6	[17]
TlO_2(anatase) + CH_2C1_2	575	>1	80	3.5	[17]
$FePO_4/SiO_2$	525	1	40	0.04	[18]
$FePO_4$ + $LaPO_4$	680	3.7	30.3	1.2	[19]
Oxides Ce, Mo, V, Fe, Co + HCl (mol mol^{-1} CH_4)	450–600			15.0	[20]
SiO_2 + Fe, Mo, Ni, Mg, Bi oxides	650	8.9	86.5	7.5	[21]
MoO_3 (2%)/SiO_2; oxidizing agent N_2O + H_2O_{steam}	550	26.0	18.8	4.9	[22]
The same without steam	550	4.0		2.4	[22]
Bi_2O_3–SnO_2, oxidizing agent N_2O + H_2O	550	2.6	92.2	2.4	[23]
ZnO/SiO_2	650	80	43.0	3.6	[24]
Mg_3P0_4	650	0.45	26		[25]
Fe–Nb–B–O	800	2.7–14	70–80		[26]
$Fe_2(Mo0_4)_3$	700	7.2	30.3	2.2	[27]
MoO_3/Fe_2O_3; 0.5 MPa	700		83.6	22.5	[28]
MoO_3/SiO_2	550–600	1.0–3.3	50–83.4	0.8–1.6	[29]
The same	600	2.6	100	2.6	[30]
V_2O_5/SiO_2	650	0.06	68		[31]
SiO_2 + MoO_3–Sn–P	550	7.2	64.8	5.0	[32]
SiO_2–Al–P–Mo	650	12.5	6.5	8.1	[33]
Sr/La_2O_3 + MoO_3/SiO_2 (or Sr/La_2O_3 + SiO_2)	630	6.7	28		[34]
K_2MoO_4/SiO_2	650	1.3	32		[35]
B_2O_3–BeO/SiO_2	650	2.8	58	4.8	[36]
$Cu_{0.01}Fe_{0.01}Zn_{0.98}O$	550	0.02	43		[37]
Aluminosilicate	750	1.0	79.6		[38]
Auminosilicate + $Ce(PO_3)_3$ (2%) + P_2O_5 (0.05%)	750			2.6	[38]
Decationized zeolite, Al/Si = 68	400	25		Σ 10	[39]
$H_3PMo_{12}O_{40}/SiO_2$ + CH_2Cl_2 or $CC1_4$	525	12	32		[40]
Heteropoly acid (Mo : Co = 10 : l)/SiO_2	600–650	20–22	65–84	14–17	[41]
Heteropoly acid (Mo : Zr = 10 : 1)/SiO_2	650	7.6–14.3	72.7–83.9	14–17	[42]
V_2O_5/SiO_2 with recycle of CH_4		89	56	50	[43]
P–MoO_3		5.8	90		[44]
Bronze grid (oxidizing agent CO_2)	380–460		100		[45]

large value of this difference for methane oxidation into formaldehyde (70 kJ mol^{-1}) gives no way of achieving a high yield. This value also indicates that methanol formed from methane must be readily oxidized into CH_2O. With the second calculation procedure used [11], it was concluded that, in the gas phase, only the oxygen conversion of methane into synthesis gas at high temperatures has no thermodynamic limitations.

Results of tests of various catalysts in steam conversion of methane into formaldehyde are listed in the table [12–45]. It can be seen that formaldehyde has been obtained on widely diverse catalysts, with mostly low yields and

high selectivity obtained at small degrees of conversion. No logical recipes follow from this table. However, four groups of catalysts can be distinguished; Mo- or V-containing supported oxide catalysts, Fe-containing oxide catalysts, acid-type catalysts, and, finally, a new group of catalysts, heteropoly acids supported for the most part by SiO_2. It is in the last case that the yield of the target product was substantially raised, to 14–17%, at a conversion of 20–23% and selectivity of 65–84%. However, no further reports on studies of this reaction in the presence of molybdenum-cobalt(zirconium)poly acids could be found in the literature.

As regards other results presented in the table, the following comments should be made. First, methane was oxidized with nitric acid [46] or nitrogen oxides [47]. For example, it was shown that a minor amount of nitric acid vapor acts as an effective catalyst: a 4% conversion of methane into formaldehyde is reached at 700–750°C in 0.5 s. A minor amount of HCl also facilitates interaction between methane and oxygen in the presence of tin, aluminum, and iron phosphates [48]. However, the best results were obtained with heterogeneous catalysts in the presence of nitrogen oxides [47]. The activation energy of such a reaction is about 170 kJ mol^{-1} [49]. It was noted in [50] that it is better to oxidize methane with pure oxygen, rather than with air, especially in the presence of nitrogen oxides. In conversion of a mixture containing oxygen and methane in a ratio $O_2 : CH_4 = 1.6 : 10$ (vol/vol), the yield of formaldehyde at 570°C was as high as 16%.

Only nearly 50 years later, it was demonstrated [51] that SiO_2, and not Al_2O_3, exhibits a noticeable activity in formaldehyde formation, and this is accounted for by the high rate of the successive deep oxidation of formaldehyde on aluminum oxide. The positive role of hydrogen chloride was attributed to its ability to poison centers of deep oxidation of CH_2O into CO_2 [52]. Introduction of dichloromethane into the reaction zone resulted in a higher process selectivity. The best conversion, but not selectivity, was achieved on the Fe_2O_3–Cr_2O_3–Al_2O_3 catalyst [14].

Strange as it was, formation of formaldehyde in a more than 60% yield has been observed on a MgO catalyst for oxidative condensation of methane at a short time of contact [14]. It is occasionally believed that an increased yield of formaldehyde can be obtained on catalysts with enhanced acidity, e.g., on tin and silicon pyrophosphate, as well as on an aluminosilicate treated with orthophosphoric acid [53, 54]. It has been shown that difficultly reducible salts are the best phosphate catalysts. It was found in this case that, for the example of magnesium salts, the yield of the target product grows with the content of phosphorus in the phosphate.

Studies have been performed with the use of various salts and supports. In particular, aluminosilicates containing 10–11% Al_2O_3 and additions of Fe, Zr, V, Ce, Cr, and Bi oxides have been examined [37–39]. The yield of formaldehyde at 750°C on an aluminosilicate modified with 2% cerium phosphate and 0.05% phosphorus pentaoxide was 2.6 times that on a pure support [39]. Introduction of dimethyl ether into the reaction zone made it possible to lower the reaction temperature by 100°C (to 650°C) and to raise the yield of CH_2O to 5–5.6%, which may be due to decomposition of the ether itself. Use of methane recirculation can raise the yield of formaldehyde to 50% [44]; however, the necessary recirculation ratio is unknown. The practicality of such a technique is doubtful.

As regards iron-niobium catalysts [55], the following can be noted. $FeNbO_4$, $FeNb_{11}O_{29}$, FeNbBO (degree of oxidation exceeding 3+), and B_2O_3 phases were found by X-ray photoelectron spectroscopy (XPS) on the surface of catalysts of this kind. A study of catalysis on separate phases demonstrated that $FeNb_{11}O_{29}$ is a catalyst with the highest selectivity (30.4% at 750°C) and the FeNbO phase is the most productive (yield 1.84%). The activation energy of the reaction of methane oxidation into formaldehyde on this catalyst is 250 kJ mol^{-1}. In a study of the catalytic activity of $Fe_2(MoO_4)_3$, together with that of Mg, Al, Ga, In, Sc, and Cr molybdates, a selectivity of 30.4% has been revealed [56, 57], whereas in other cases, it was less than 20%. It was shown that minor additions of Li^+, Zn^{2+}, and Ce^{3+} somewhat improve the process selectivity.

Also, the selectivity of methane on phases of the type $Li_{0.5}Fe_{0.5}MoO_4$ has been studied [58], with a selectivity of 96% at 650°C observed. As the stoichiometric subscript is varied, the composition of the reaction products changes and CO_2 and ethane are formed; however, the reaction rate increases with the concentration of iron. It has been shown [28] that the yield of formaldehyde on the MoO_3–Fe_2O_3 catalysts is as high as 22.5% at a selectivity of 83.6%, temperature of 700°C, pressure of 0.5 MPa, and CH_4 : O2 ratio of 2 : 1. However, such a result can only be obtained under particular conditions unspecified by the author. The higher activity and selectivity of the $Cu_{0.01}Fe_{0.01}Zn_{0.98}O$ catalyst (produced by addition of 1% CuO and Fe_2O_3 to ZnO), compared with pure ZnO, was attributed to a combination of the redox properties

of Fe^{2+}/Fe^{3+} and Cu^{+}/Cu^{2+} pairs with the Lewis acidity of Fe^{3+} [59]. At the same time, the author of review [60] came to a conclusion that the maximum yields of formaldehyde on iron-containing catalysts do not exceed those in an empty steel reactor.

A large number of oxide catalysts supported by pumice stone have been studied at a pressure of 5 MPa and a 50-fold excess of methane [61]. In particular, the Ag_2O (6.7%)–MoO_3 (1%) catalyst supported by pumice stone made it possible to obtain an overall selectivity of 79% with respect to formaldehyde and methanol. It was shown in [36] that, with various oxide deposited onto SiO_2 in an amount of 9.2%, the maximum conversion at 650°C and $CH_4 : O_2 = 1 : 1$ is observed for Ga_2O_3 and Bi_2O_3, i.e., for metal oxides with a medium electronegativity. The dependence of the conversion on the electronegativity shows an extremal behavior with a maximum for gallium oxide. By contrast, the selectivity exhibits a steady tendency to rise as the electronegativity of the additive element increases. The oxides can be arranged in order of decreasing selectivity as follows: P_2O_5, WO_3, B_2O_3 (>60%) > Sb_2O_3, Nb_2O_3, Al_2O_3, MgO (>30%), i.e., the acidic oxides are more selective. A combination of more selective oxides with those having a higher activity has yielded the B_2O_3–BeO/SiO_2 catalyst [36].

The largest number of studies has been performed with the MoO_3/SiO_2 system, because its presence provides better results than other catalytic systems: 85% selectivity at a conversion of 3–4% and 30% selectivity at a conversion of 7%. On pure (without support) MoO_3, formaldehyde is formed in trace amounts. The acting substrate has not always been studied in the form of MoO_3; occasionally, other molybdenum compounds have also been considered. For example, the oxidation of methane on K_2MoO_4 has been studied on various supports: SiO_2, Al_2O_3, TiO_2, MgO, and ZSM-5 zeolite [35], and the system K_2MoO_4/SiO_2 proved to be more selective (32%). It has been found that chromium and copper oxides improve the selectivity [36, 62], but this evidence is contradictory. For example, it was demonstrated in [63] that iron, chromium, cobalt, and sodium diminish the selectivity of formaldehyde formation as compared with the purely molybdenum catalyst. Addition of tin and phosphorus raises the conversion and selectivity, respectively [32]. With a combined Sn–P-MoO_3/SiO_2 catalyst, a selectivity of 64.8% has been obtained at a conversion of 7.2%.

A 80% selectivity at a low conversion has been obtained on a $MoCl_5/R_4Sn/SiO_2$ catalyst in which the Mo–O group was substituted with $Mo{=}CH_2$ [64]. The suggestion to introduce nitrogen oxides into the reaction mixture was not forgotten, either, in tests of Mo/SiO_2 and V/SiO_2 [65]. The maximum yield of CH_2O was 4% at a conversion of 4% and selectivity of 40% [66, 67]. A noticeable selectivity in methane oxidation has been observed for the $H_3[PMo_{12}O_{40}]$ heteropoly acid and its salts supported by silica gel, in the presence of N_2O (80%, conversion 2%) [68]. A relationship between the acidity of a catalyst and the formaldehyde yield has been observed [69]. The suggestion to test this acid appeared after it was demonstrated that a silicomolybdenic acid was formed at the surface of SiO_2 containing 1–5% Mo. This acid has been synthesized by an independent method and deposited onto SiO_2 [71], with the activity of the formulation increased in the presence of chlorine-containing additives, such as CH_2Cl and CCl_4, and a conversion of 12% obtained at a selectivity of 32% [72].

In tests, a catalyst of composition Sr/Las_2O_3–MoO_3/SiO_2 was divided into two layers: Sr/La_2O_3 and MoO_3/SiO_2. At 630°C, the yield of formaldehyde was higher than that on each of the phases separately or on their mechanical mixture, but the selectivity was lower. This means that the first layer initiates the reaction, and formaldehyde is formed in the second layer [73].

A study of vanadium-containing catalysts has shown that V_2O_5/SiO_2 is more active at low temperatures, and MoO_3/SiO_2, at high temperatures [74]. In all cases, the selectivity decreases in a direct proportion to the increase in conversion, the typical yield of formaldehyde on catalysts of this kind is 1–1.2%. It is notable that V_2O_5/SiO_2 exhibits a noticeable activity at temperatures 80–100°C lower than those for the molybdenum analog [75], with the activation energy of the reaction estimated to be 88 kJ mol^{-1}.

It is maintained [76] that a 20% selectivity at a 1% conversion can be obtained with the so-called membrane V_2O_5/SiO_2 catalysts. Also worth mentioning, among unconventional methods employed in methane oxidation, is the effect of the mechanical activation on the catalytic properties of molybdenum and vanadium catalysts [77, 78]. On subjecting mechanical mixtures $Mo + SiO_2$, $MoO_3 + SiO_2$,$V + SiO_2$, and $V_2O_5 + SiO_2$ to grinding in a ball mill or to a high pressure, the side reaction of deep oxidation did not occur. The selectivity of the reaction on the molybdenum catalyst increased to 100% at a methane conversion of 2.1%, and that on the vanadium-containing catalyst was 99% at a conversion of 2.5%. Supporting the components with SiO_2 before the grinding had no

effect on the selectivity of the reaction, even if they were ground afterwards. Electronic spectroscopy and electron diffraction analysis demonstrated that "encapsulation" occurs under the mechanical treatment conditions, i.e., the active phases are coated with a silica gel sheath.

Studies of the last 7–15 years largely consist either in kinetic analysis and construction of a mathematical model of methane conversion into formaldehyde [79, 80], or in a purely academic examination of the reaction, e.g., by employing the method of nanocatalysis in a vibrating fluidized bed [81], performing the reaction in supercritical water [82], and using enzymes [83] or plasma glow discharge [84]. However, catalysts of a somewhat different composition have also been considered, e.g., SnSrO and Mn/SnO_2 [85], $BaNixAl_{12-x}O_{19-x}$ and $LaAl_{5/6}N_{1/6}O_3$ [86] rhenium oxide on SiO_2 [87], and even grafted catalysts $Mo(acac)_2O_2$ on HZSM-5 [88], as well as the reaction in the presence of nitrogen oxides [89]. The catalysts have been studied using various physicochemical methods [90] and even a quantum-chemical evaluation of the SiO_2 surface has been made by modeling it with a helical $Si_6O_{18}H_{12}$ molecular cluster [91].

In two studies, heteropoly acids were not left aside. For example, the reaction of methane oxidation to formaldehyde has been catalyzed with an aqueous solution of a potassium salt of di-iron-substituted silicon tungstate, γ-$SiW_{10}[Fe(OH)_2]_2O_{38}^{6-}$ [92]. Mono- and tri-iron-substituted derivatives are substantially less active and nonselective. It is noted that the "di-iron-center" is effective for selective oxidation by hydrogen peroxide. The use of heteropoly acid complex catalysts based on dodecaoxo metallic complexes having Fe^{3+} and Cr^{3+} in the inner sphere has been reported [93]. It is noted that the catalysts are also promising for industrial use.

The continuation of research in this area is dictated not so much by the low yield of formaldehyde as by the necessity for improving the economical parameters, because it is believed [94] that combination of the processes of methane oxidation to formaldehyde and production of synthesis gas by using the heat released in the first reaction are beneficial and advisable.

MECHANISM AND SPECIFIC FEATURES OF THE KINETICS OF THE METHANE OXIDATION REACTION

According to [15], the chemical nature of the catalytic oxidation of methane can be represented by the following scheme:

$$CH_4 \xrightarrow{[O_2]} [CH_3^{\bullet}] \begin{cases} \xrightarrow{O_2} CH_2O \rightarrow CO + H_2 \xrightarrow{O_2} CO_2 + H_2O, \\ \xrightarrow{[O_2]} C_2H_6 \xrightarrow{O_2} C_2H_4 + H_2O. \end{cases}$$

It has been noted [2] that the process selectivity steeply decreases as the conversion becomes higher. However, the selectivity can be changed by varying the reaction conditions. For example, raising the volumetric flow velocity of the mixture $CH_4 : O_2 : Ar = 6 : 1 : 6$ on a MgO catalyst from 1000 to 48000 h^{-1} leads to 65% selectivity of formaldehyde formation at a 9% conversion of oxygen, and to a decrease in selectivity to almost zero at a 11% conversion. As the conversion increases, the yield of ethylene and carbon dioxide grows. It is believed that both reactions compete in this scheme. The first reaction is first-order with respect to $[CH_4]$ or $[CH_3^{\bullet}]$, and the second, second-order (recombination of radicals). It is for this reason that the reaction pathway toward formaldehyde is more probable at high volumetric loads. An elevated pressure is undesirable in this process, because it directs the reaction toward methanol formation.

In methane oxidation on iron molybdate (525–700°C, $P_{CH_4} = P_{O_2} = 20$ kPa), the selectivity of CH_2O formation decreases and the selectivity CO increases as the conversion becomes higher [57]. The total sum of the selectivities remains constant, which confirms the above scheme. The same authors studied under the same conditions the oxidation of methanol and demonstrated that formaldehyde is the primary oxidation product and then carbon oxides are formed. This indicates that methanol can be formed as a precursor of CH_2O in catalytic oxidation of methane by the scheme $CH_4 \rightarrow CH_3OH \rightarrow CH_2O \rightarrow CO \rightarrow CO_2$. No formation of C_2-hydrocarbons was observed and, in the authors' opinion, the reaction occurs at the catalyst surface.

The simultaneous formation of formaldehyde and methanol, observed by various researchers, is regarded as confirmation of the scheme of successive generation $CH_3OH \rightarrow CH_2O$, but formaldehyde is formed in a larger amount [2].

Additional formation of hydrogen and C_2-hydrocarbons is observed on iron, zinc, and zirconium phosphates [57]. On this system, the selectivity of formation of formaldehyde and C_2-hydrocarbons decreases as the contact duration becomes shorter. The oxygen pressure affects this process only slightly, but the selectivity ratio SCH_2O/SCH_2 linearly increases as the O_2 pressure is raised. In the authors' opinion, such dependence may

serve as evidence in favor of the existence of a common intermediate for oxidative condensation of methane and for oxidation of CH_4 into CH_2O. By the intermediate are understood methyl radicals, on which different authors, on the whole, agree.

There are data [95], according to which the selectivity of formaldehyde and carbon dioxide formation on molybdenum-containing oxide catalysts varies identically, i.e., parallel pathways of formation of these products are possible in direct oxidation of methane. In another study of methane oxidation on a V_2O_5/SiO_2 catalyst [31], in which the isotope exchange of tracer atoms is analyzed and the response method is employed, parallel pathways of methanol and formaldehyde formation are taken into consideration together with the consecutive mechanism.

It was found in one of recent studies [90] that the main products formed in oxidation of methane on $FePO_4/SiO_2$ at 500–690°C, volumetric load of 25000–65000 h^{-1}, and $CH_4 : O_2 = 1 : 1$ are formaldehyde and carbon dioxide, with methanol as an admixture. It was found that the catalytic activity strongly depends on the amount of iron phosphate, taken in concentrations of 2–16 wt %. The best result was obtained on 2% $FePO_4$, with the output capacity in terms of CH_2O and CH_3OH reaching values of 622 and 25 g kg_{cat}^{-1} h^{-1}, respectively. The relationship between the selectivity and conversion led the authors to conclude that methane is oxidized directly to formaldehyde and methanol, and then to CO and CO_2.

It has been shown in a study of the reaction on SnO_2 that the rate of the catalytic reaction, dependent on the partial pressures of CH_4 and O_2, is 0.47 ± 0.02 and 0.07 ± 0.02 m^{-3} min^{-1} at methane and oxygen pressures of, respectively, 0.4–1.0 and 0.5–20 kPa at 440–500°C [96].

It has been shown in a study of methane oxidation on a supported silica catalyst at 575–625°C at partial pressures of reagents, characteristic of these temperatures, that, irrespective of the pathway, the reaction has positive orders with respect to all the reagents and the manner in which the partial pressure of oxygen varies points to its chemisorption [97]. Based on this fact, the authors conclude that the chemisorption of oxygen on reduced centers occurs at a rate comparable with the rate of substrate oxidation and, consequently, can limit the oxidation rate. Self-inhibition is observed in CO oxidation as P_{CO} increases. A model is suggested in which CO and O_2 compete for surface oxygen vacancies.

The kinetics of the reaction has been studied on the same catalyst in the temperature range under dynamic equilibrium conditions by measuring in situ the chemisorption of oxygen. A pseudo-first order with respect to methane and zeroth order with respect to oxygen has been observed [80]. It was noted that the density of reduced centers of the catalyst is proportional to a square root of the P_{CH4}/P_{O_2} ratio. The rate-determining stage is the activation of the C–H bond in the CH_4 molecule (E_{red} = 142 kJ mol^{-1}), whereas "replenishment" with oxygen is a nonactivated stage of the reaction (E_{ox} = 20 kJ mol^{-1}). The process is described by the Langmuir–Hinshelwood model in terms of the two-band dissociative activation mechanism.

Other authors [79] have studied the effect of oxygen and methane on the density of reduced centers on the same catalyst in a batch reactor with flow circulation under dynamic equilibrium conditions and estimated the reaction orders with respect to CH_4 and O_2 to be 0.9 and 0.2, respectively. The dependence of the density of reduced centers on the ratio between the partial pressures of the reactants was determined, as it was also done in [80].The formal kinetics was also described in terms of the Langmuir–Hinshelwood model.

In [98, 99], the reaction course, and primarily the formation and consumption of methyl radicals, were kinetically monitored. It was demonstrated that intense additional formation of Me leads to the highest yields of the target products (formaldehyde, methanol, ethane, and ethylene, depending on the reaction pathway). It is assumed that the role of a catalyst in high-temperature oxidation of methane is determined by its ability to generate and remove methyl radicals. It is also noted that an effective catalysis requires that the rate of the catalytic generation of methyl radicals should exceed by at least five to six orders of magnitude the rate of their gas-phase formation. In addition, there exists the maximum yield of the principal products, which cannot be exceeded by further raising the generation rate of intermediate radicals. It is noted that just the surface oxygen O_s promotes formation of $CH_3^{\cdot}$, with the subsequent repeated oxidation in the catalytic cycle:

$$CH_4 + O_s \rightarrow CH_3^{\cdot} + OH_s,$$

$$4OH_s + O_2 \rightarrow 2H_2O + 4O_s.$$

The high and close values of the activation energies of the occurring reactions (oxidation, dimerization) (~200 kJ mol^{-1}), their proportionality to the partial pressure of methane [(w/k)P_{CH4}], and manifestation of the kinetic isotopic effect ($k_{CH_4}/k_{CD_4} > 1$) validate the assumption that

the rupture of the C–H bond in these oxidation processes on the catalyst surface is, indeed, the rate determining stage of the whole process.

The effect of the catalyst surface area by BET on the methane oxidation has been studied and it was shown that the specific surface area is important not only for activation of methane, but also for decomposition of reactive intermediates. It is assumed that formaldehyde and carbon dioxide are primary products, and CO is a secondary product of decomposition of CH_2O and hydrocarbons. The large surface area led to decomposition of hydrocarbons to CO, whereas on catalysts with a small surface area, this side reaction is partly inhibited by the simultaneous formation of C_2-hydrocarbons. However, the selectivity of the main reaction decreases as the surface area becomes smaller and this surface activates methane to a considerably greater extent than does the gas-phase thermal shock.

Some researchers believe [101] that alkanes are activated by the so-called heterogeneous-homogeneous mechanism. This particularly refers to oxidation of methane, which, in contrast to other hydrocarbons, is not adsorbed on the catalyst surface at the reaction temperature. It is activated upon an impact against the surface, being transformed into a methyl radical, which is desorbed and, as a result of a secondary interaction with various forms of oxygen of with the OH group on the surface, forms a chemisorbed methoxy radical.

It was shown in [8] that the selectivity of formaldehyde formation depends on the concentration of the gas-phase oxygen: the higher this concentration, the lower the selectivity, with an increase in the content of carbon oxides observed. The authors write that "catalytic anisotropy" is observed in oxidation of the intermediates CH_2O, CH_3OH, and CO under the conditions of the main reaction. Full oxidation of products formed in partial oxidation occurred more favorably on catalysts with (010) basal faces. Runs with oxidation of formaldehyde as the starting product yielded mostly carbon dioxide in a reactor containng no catalyst. This means that further oxidation of CH_2O may occur in the gas phase. With a MoO_3 catalyst present, an increase in the conversion into carbon dioxide was observed. Additional experiments demonstrated that CO oxidation to CO_2 in the absence of a catalyst almost does not occur at all. In oxidation at 650°C, methanol was completely converted to formaldehyde, which led the authors to suggest the consecutive conversion scheme $CH_4 \rightarrow CH_3OH \rightarrow CH_2O$. Interestingly, the same conclusion follows from a quantum-chemical calculation by the semi-empirical MOPAC-PM3 method of the model of a reaction on SiO_2 [91]. In addition to the aforesaid, the study [102] should be mentioned, in which the structural specificity of MoO_3 in methanol oxidation was analyzed and it was shown that CH_2O and CO are formed from methoxy groups mostly at the terminal Mo=O center, whereas bridge Mo–O–Mo centers are responsible for products of the type of dimethyl ether. The authors found that "shear" faces appear at high temperatures and promote oxygen diffusion from the bulk toward the surface.

MECHANISM OF CATALYTIC OXIDATION OF METHANE TO FORMALDEHYDE

Semenov and co-workers have suggested [103] a mechanism of homogeneous oxidation of methane, which is operative at temperatures below 500°C and only at small reactant conversions:

$$CH_4 + O_2 \longrightarrow CH_3 + HO_2^{\bullet},$$
$$CH_3^{\bullet} + O_2 \longrightarrow CH_2O + HO^{\bullet},$$
$$HO^{\bullet} + CH_4 \longrightarrow H_2O + {}^{\bullet}CH_3,$$
$$HO^{\bullet} + CH_2O \longrightarrow {}^{\bullet}CH{=}O + H_2O,$$
$${}^{\bullet}CH{=}O + O_2 \longrightarrow CO + HO_2^{\bullet},$$
$$HO_2^{\bullet} + CH_4 \longrightarrow H_2O_2 + CH_3^{\bullet},$$
$$HO_2^{\bullet} + CH_2O \longrightarrow H_2O_2 + {}^{\bullet}CH{=}O,$$
$$HO^{\bullet} \longrightarrow \text{loss at the wall.}$$

The most difficultly occurring stage in the suggested scheme of methane oxidation is the formation of the primary methyl radical from methane and oxygen, which requires 230–235 kJ mol^{-1}. A comparatively high activation energy of 168 kJ mol^{-1} is required by chain branching reactions, i.e., reactions with active intermediate species, which lead to an increase in the number of free radicals. The reactions of chain growth occur easily with E_a of 20 to 45 kJ mol^{-1}.

Several decades later, several mechanistic models of the process of homogeneous methane oxidation were suggested. All the schemes [104, 105] assume that the chain originates in the stage of formation of the methyl radical, with an activation energy exceeding 200 kJ mol^{-1}. Any stages involving free radicals serve for chain continuation. The following stages lead to chain branching:

$$H_2O_2 + M \longrightarrow 2HO^{\bullet},$$
$$CH_2O + O_2 \longrightarrow HO_2^{\bullet} + CHO^{\bullet},$$
$$CH_3OOH \longrightarrow CH_3O^{\bullet} + HO^{\bullet},$$

Chain termination may occur via loss of active species at reactor walls, as well as in the stages

$$CH_3^{\bullet} + H^{\bullet} \longrightarrow CH_4,$$
$$2CH_3^{\bullet} \longrightarrow C_2H_6.$$

Under the process conditions, formaldehyde and methanol formed in methane oxidation undergo further transformations to deep oxidation products, CO_2 and H_2O, with the result that the yield of formaldehyde at 500–600°C does not exceed 0.5% [103]. The yield of methanol may be as high as several percent. To raise the yield, various ways to activate the first stage of the reaction have been used: addition of nitrogen oxides or halogen derivative, treatment with electric discharge or ionizing radiation [106, 107], but all these methods proved to be poorly efficient.

The above data are largely of only historical interest. According to modern concepts based on results of numerous studies, two types of mechanisms are distinguished for reactions of this kind: free-radical and molecular. The former, as applied to the reaction of methane oxidation, are distinguished into a group of "heterogeneous-homogeneous" reactions in which the selectivity is predominantly determined by gas reactions. The latter are heterogeneous reactions whose selectivity is governed by surface processes. In Krylov's opinion [2], the fact that free radicals are found under the conditions of catalytic oxidation of methane to formaldehyde is the main evidence in favor of the heterogeneous-homogeneous mechanism. However, Margolis, who was one of the first to discover the formation of CH_3O_2 radicals, believes in just the opposite: an increase in the number of free radicals favors a nonselective process and leads to a decrease in the yield of formaldehyde [11].

Addition of C_2H_6 to the CH_4–O_2 mixture makes higher the selectivity of methane oxidation to formaldehyde at 560–640°C on SiO_2 and diminishes the yield of carbon oxide. It is believed that this is due to an increase in the amount of methyl radicals formed from ethane. Under these conditions, $CH_3^{\bullet}$ radicals are further transformed to $CH_3O_2^{\bullet}$ and $CH_3O^{\bullet}$. In [108], a correlation was noted between the yield of the radicals $CH_3O_2^{\bullet}$ and $CH_3O^{\bullet}$ and that of CH_2O under the conditions of methane oxidation on SiO_2. As temperature is raised, the yield of formaldehyde and the $CH_3O_2^{\bullet}$ concentration pass through a maximum at 640°C. Deposition of hydrogen peroxide onto silica gel also leads to an increase in the yield of formaldehyde and free radicals [109].

The most widely accepted opinion is that methyl radicals are formed in the reaction of CH_4 with the surface oxygen (Os). For example, $CH_3^{\bullet}$ radicals are formed on an iron-boron-niobium catalyst in the primary interaction of CH_4 with O_s, and formaldehyde is produced by secondary interaction of $CH_3^{\bullet}$ with O_s [26]:

$$CH_4 + O_s \longrightarrow CH_3^{\bullet} + HO_s,$$
$$CH_3^{\bullet} + O_s \longrightarrow CH_2O + 0.5H_2,$$
$$2HO_s \quad H_2O + O_s.$$

The lifetime of the active O_s oxygen (O– or O_2^-) reacting with methane is 5–16 s.

In the opinion of the authors of [110], who studied the mechanism of methane oxidation on the V_2O_5/SiO_2 catalyst with the use of $18O_2$, $CH_3^{\bullet}$ radicals are, indeed, formed in the first stage and further react with oxygen to give formaldehyde:

$$CH_3^{\bullet} + {}^{18}O_2 \longrightarrow CH_2{}^{18}O + HO^{\bullet}.$$

The involvement of methyl radicals in the formation of oxygen-containing compounds has been confirmed by an independent method in thermal decomposition of methane [111]. It was demonstrated by means of IR spectroscopy that $CH_3^{\bullet}$ radicals generated on the V_2O_5/SiO_2 catalyst form methoxy groups on the surface. In this case, it was found using the EPR method that the degree of oxidation of the vanadium contained in the catalyst decreases to V^{4+}. According to thermographic data, the surface methoxy groups decompose to formaldehyde or react with water to give methanol, which is represented by the authors of [111] as

$$(CH_3O)^- \cdots \longrightarrow CH_2O + OH^-,$$
$$(CH_3O)^- + H_2O \longrightarrow CH_3OH + OH^-.$$

It was demonstrated in the same study that methanol starts to be formed at 300°C, and formaldehyde, at 400°C, i.e., the reaction of methoxy groups with water is faster. At the same time, methanol is rapidly oxidized to formaldehyde at 400–500°C and it can be assumed that CH_3OH is an intermediate in synthesis of CH_2O. However, both products are formed at high concentrations of V_2O_5 (2–10%) from the same intermediate, $(CH_3O)^-$. These data suggest that the catalyst promotes formation

of methoxy groups, which further undergo conversion on the catalyst surface without desorption into the volume.

To the same opinion adhere the authors of [112], who studied the partial oxidation of methane on a double-layer catalyst constituted by Sr/La_2O_3 (generates $CH_3^{\cdot}$ radicals) and MoO_3/SiO_2 (catalyzes the subsequent heterogeneous reactions). An interesting observation made in [112] served as a foundation of the modern concept of the mechanism by which formaldehyde and its precursor are formed. For example, it is known that methane oxidation to formaldehyde occurs at 500–600°C, i.e., below 650°C, when the equilibrium

$$CH_3^{\cdot} + O_2 \rightleftarrows CH_3OO^{\cdot}$$

is shifted to the right, which led the authors to conclude that formaldehyde can possibly be formed from the peroxide radical.

As regards nitrogen dioxide, a well-known and good-performance additive to the reaction zone of partial oxidation of methane, it is known that NO_2 promotes hydrogen abstraction from CH_4 and generation of $CH_3O^{\cdot}$ [113]. The above reaction of generation of the methoxy radical from the peroxide radical $CH_3OO^{\cdot}$ requires high energy expenditure, whereas in the presence of NO_x, the activation energy is substantially lower. On the basis of a kinetic analysis of the process, the following chemism of methane conversion in the presence of nitrogen dioxide was suggested:

$$CH_4 + NO_2 \longrightarrow CH_3^{\cdot} + HNO_2,$$
$$CH_3^{\cdot} + NO_2 \longrightarrow CH_3O^{\cdot} + NO,$$
$$Mo^{6+}\text{–}O^{-} + CH_4 \longrightarrow Mo^{6+}\text{–}OH + CH_3^{\cdot},$$
$$Mo^{6+}\text{–}O_2^{2-} + CH_3^{\cdot} \longrightarrow Mo^{5+}\text{–}OCH_3^{-},$$
$$Mo^{5+}\text{–}OCH_3^{-} + Mo^{6+}\text{–}O_2^{2-} \longrightarrow Mo^{5+}OH^{-} + Mo^{5+}[\ ]^{-} + CH_2O,$$

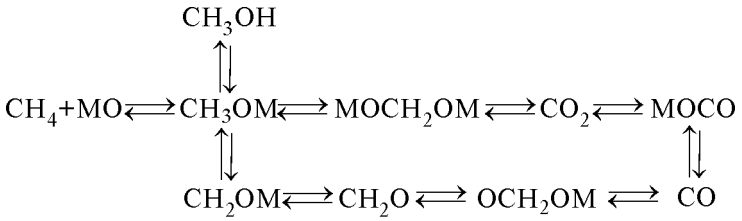
Because the amount of activated methane in the reaction substantially exceeds that of NO_2 added, it was suggested that nitrogen dioxide is recycled as a catalyst.

The mechanism of action of chlorine-containing activators consists, according to [17], in that the $CH_3^{\cdot}$ concentration in the gas phase increases upon thermal decomposition of dichloromethane by the reaction

$$CH_4 + Cl^{\cdot} \longrightarrow CH_3^{\cdot} + HCl.$$

To another mechanism of oxidative conversion of methane belong transformations unrelated to generation of radicals. In this case, the activity of catalysts is determined by the rate of hydrogen abstraction from methane [7]. For cations with high electronegativity (basic oxides), the large negative charge on the oxygen of the oxide favors hydrogen abstraction. By contrast, cations with low electronegativity or acidic oxides (P_2O_5, B_2O_3, MoO_3, V_2O_5) with a small charge on the oxygen atom facilitate addition of an oxygen molecule to CH_{4x}^{-} to give formaldehyde.

Upon a study of the oxidation kinetics of methane, methanol, and formaldehyde at 370–650°C on MoO_3/SiO_2 and V_2O_5/SiO_2, a detailed parallel-consecutive scheme was suggested and a macrokinetic model satisfactorily describing the experiment was constructed [114]:



Here, the limiting yields of formaldehyde are accounted for by the fact that it is an intermediate in oxidation to CO. By contrast, CO_2 is formed by two pathways: directly from methane and via oxidation of CO in the gas phase. In the first case, the yield of CO_2 is independent of the degree of methane conversion (MoO_3 catalyst), and in the second, it grows with the conversion (V_2O_5 catalyst).

Let us consider the following mechanism of methane oxidation, attributed by the authors of [2] to the radical type. Here, the main issue is the source of oxygen in the oxygenate: oxygen from the gas phase or lattice oxygen. For example, it was shown in [26] that the oxygen of the Fe–Nb–O catalyst is firmly bound and is not exchanged for $^{18}O_2$ from the gas phase under the conditions of catalysis. By contrast, a rapid exchange

of oxygen between the Mo–O group and CH_2O has been observed on the MoO_3/SiO_2 catalyst in methane oxidation [115], which indicates that the mechanisms of oxidation on these catalysts are different. A substantial acceleration of the exchange of $^{18}O_2$ in the presence of CH_4 has also been observed on V_2O_5/SiO_2, which, in the opinion of the authors of [116], shows that the lattice oxygen is involved in the formation of products of partial and full oxidation of methane.

Active centers of Mo- and V-containing catalysts have for the most part been studied by EPR spectroscopy, which is due to the easy reduction of Mo^{6+}=O and V^{5+}=O groups to, as the authors believe, Mo^{6+}–O– and V^{5+}–O^- radical centers, and further to Mo^{5+}–O^- and V^{4+}–O^- (or Mo^{5+}–OH^- and V^{4+}–OH^-). Further involvement of these centers in catalysis is commonly represented as [2, 117]:

$$Mo^{6+}\text{–}O^- + CH_4 \longrightarrow Mo^{6+}\text{–}OH + CH_3^{\bullet},$$
$$Mo^{6+}\text{–}O_2^{2-} + CH_3^{\bullet} \longrightarrow Mo^{5+}\text{–}OCH_3^-,$$
$$Mo^{5+}\text{–}OCH_3^- + Mo^{6+}\text{–}O_2^{2-} \longrightarrow Mo^{5+}OH^- + Mo^{5+}[\ ]^- + CH_2O,$$

which seems to be highly questionable because of the confusion regarding the charges and ways of their representation and also species of the type Mo^{6+}–O_2^{2-}, heaven-knows-wherefrom taken by the authors, judging from the text presented above. However, in our opinion, the direction of thought is correct and, on putting the electron transfers in order (which is beyond the scope of the review), the mechanism will be ion-radical, rather than radical, suggested by the authors of [2].

The nonselective oxidation occurs by the reaction [117]:

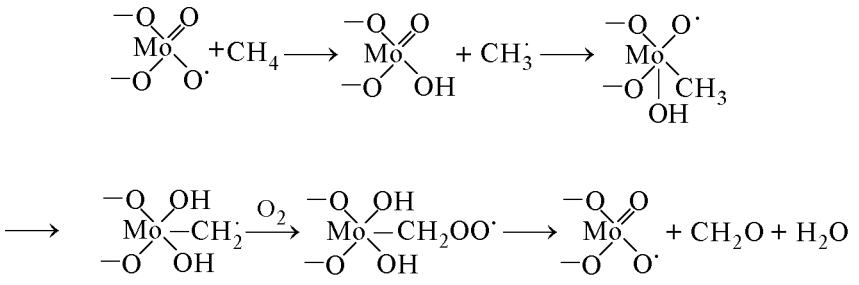
$$8Mo^{6+} + 4O^{2-} + CH_4 \longrightarrow 8Mo^{5+} + 2H_2O + CO_2.$$

Thus, the single-electron transfer from O^- centers leads to CH_2O, and the two-electron transfer from O_2^{2-} centers, to CO_2. In contrast to this opinion, there exists another concept [67]: O^- and O^{2-} lead to full and partial oxidation, respectively.

According to Raman spectra [8], methane oxidation on a MoO_3 single crystal leads to formation of formaldehyde with the help of Mo=O groups on (100) lateral faces, and bridge groups on (010) basal faces cause deep oxidation. Similar conclusions have been made for supported 0.5–1.8% MoO_3/SiO_2 catalysts [118]. It was shown that a heteropoly acid with upwards directed oxygen atoms of Mo=O groups providing selective oxidation are formed on the surface. At higher MoO_3 concentrations, bridge structures responsible for deep oxidation are formed. CH_3O groups have been observed on catalysts of this type by IR spectroscopy [119].

In turn, an in situ study of V_2O_5/SiO_2 by Raman spectroscopy demonstrated that isolated V^{5+} ions are active centers [2] and their degree of oxidation remains unchanged under the catalysis conditions. In addition, it is believed that, only in the case of a vanadium catalyst, EPR spectroscopy unambiguously identifies the formation and consumption of stabilized oxygen in reduction and oxidation [120]. O^- and O^{2-} are formed in interaction of O_2 with this catalyst [121].

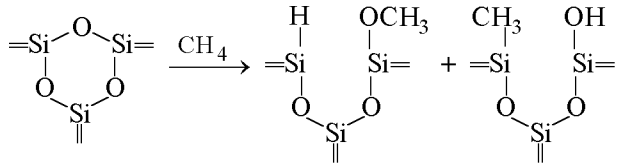
According to [120, 122], mechanochemical oxidation of the MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts yields high concentrations of Mo^{5+} and V^{4+} radical centers, which can activate methane, with its subsequent oxidation by molecular oxygen:



As already noted, the most widely used support for partial oxidation of methane (SiO_2) shows a certain amount of independent activity. This property has not been disregarded and was accounted for either by purely molecular or by radical processes. In the first case, it is assumed that all intermediate stages occur without desorption from the surface and reactions involve oxygen atoms of the substrate. The substrate oxygen is

directly involved in the formation of methyl, methoxy, and hydroxy groups, with $CH_3^{\cdot}$ radicals leading only to oxidative condensation to ethane.

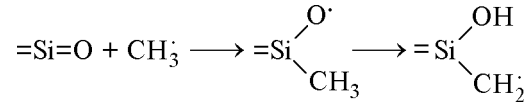
In contrast to this scheme, the high catalytic activity of deposited SiO_2 was explained in [124] by introducing the notion of certain "reduced centers" that react with oxygen from the gas phase and provide active oxygen for oxidation of methane:



It was shown in [125, 126] that high concentrations of free-radical centers can be obtained in mechanochemical grinding of SiO_2 with a concentration of paramagnetic defects of up to 1% relative to the number of surface atoms. Defects of this kind are formed in cleavage of siloxane bonds ≡Si–O–. Grinding in the atmosphere of oxygen also promotes formation of ≡Si–O–$O_3^{\cdot}$ and ≡Si–O–O–$O_3^{\cdot}$ centers. In these cases, a silicon atom is bonded to three lattice atoms of oxygen. The second type of defects, diamagnetic silicon atom, is bonded to two lattice atoms of oxygen. In this series, silicone, silanone, and siladioxirane groups have been identified by EPR, IR, and UV spectroscopies. For these groups, mechanistic approaches to interaction with methane have been developed, e.g.,

$$\equiv Si{-}O_3^{\cdot} + CH_4 \longrightarrow \equiv Si{-}OH + CH_{33}^{\cdot}$$

The reaction proceeds at a high rate even at 195°C, without any noticeable activation energy. Further, $CH_3^{\cdot}$ radicals are captured by the diamagnetic centers:



Further interaction of centers of the type $=Si(OH)CH_2^{\cdot}$ with oxygen yields formaldehyde:

$$=Si(OH)CH_2^{\cdot} + O_2 \longrightarrow =Si(OH)CH_2OO^{\cdot}$$

$$\longrightarrow =Si(OH)O^{\cdot} + CH_2O$$

The completion of the catalytic cycle requires dehydration of ≡Si–OH groups; this stage is believed to be the most difficult.

When discussing the mechanism by which formaldehyde is formed, it is impossible to disregard another possible pathway of its formation, via thermal decomposition of surface-bound methoxy groups, which occurs at 700°C [127, 128]:

$$\equiv Si{-}O{-}CH_3 \longrightarrow \equiv Si{-}H + CH_2O.$$

This reaction confirms the possibility of formation of CH_2O precursors on the surface and their subsequent conversion to formaldehyde without intermediate desorption.

Rather interesting are studies of the photochemical and radiation-induced synthesis of formaldehyde under the action of UV light and γ-radiation on the conventional catalysts and reagents. Procedures of this kind enable evaluation of the role of various parameters in catalysis. For example, up to 15% formaldehyde has been obtained by thermal desorption of γ-irradiated mixture of V_2O_5/SiO_2 with CH_4 and O_2 [129]. Here, an important issue is that CH_2O was found on the surface of the catalyst, rather than in its bulk. The formation of formaldehyde has also been observed with MoO_3/SiO_2 under UV irradiation at 180°C [130]. The yield of the target product was 0.2 μmol g_{cat}^{-1} h^{-1}, which is comparable with the best yield on this catalyst without irradiation at 570°C. Interestingly, CO and CO_2 were completely absent under irradiation and could be obtained only at higher temperatures. According to the opinion of the authors of [2], these data indicate that oxygen ion-radicals are involved in both thermal and photochemical processes, but, for unknown reason, these ions are related to radical processes.

The possibility of formaldehyde formation under UV irradiation has also been demonstrated for the example of MgO at 750°C, with the following scheme suggested [123]:

$$MgO + h\nu \longrightarrow MgO^- + e,$$

$$MgO^- + CH_4 \longrightarrow MgOH^- + CH_3^{\cdot},$$

$$Mg^{2+} + CH_3^{\cdot} \longrightarrow Mg^+CH_3^-$$

or

$$CH_3^{\cdot} + O^{2-} \longrightarrow OCH_3^- + e.$$

It is noted that formaldehyde is further formed from the OCH_3^- group. Even if the incorrectness of the scheme is left aside, it is impossible to understand why the lattice oxygen is considered to be involved.

In [2, 13], photoconversion of CH_4 and O_2 on various

oxides was studied, with two competing processes observed: formation of hydrocarbons and oxygen-containing products. Excitation by light across the energy gap of an oxide primarily leads to formation of oxygen-containing products, and excitation of impurity levels of oxides yields hydrocarbons. Dissociative photoadsorption of CH_4 leads to formation of excited OH surface groups, which causes gradual poisoning of the surface.

In the context of the specific behavior of heteropoly acids, it was of indubitable interest to analyze the most recent published data related to specific features of their structure and catalytic properties. For example, noteworthy are communications [132, 133] in which the role played by the lattice oxygen was demonstrated and it was concluded that the final stage of formaldehyde formation on heteropoly acids occurs in the crystal bulk, which suggests that the effect of the "pseudoliquid phase" takes place. Also, the influence of the size effect was observed, with the reaction selectivity increasing upon a decrease in the particle size of the active component of the catalyst to less than 100 nm. A new mechanism was suggested for the reaction of methane oxidation to formaldehyde:

$$CH_4 + M_x^{n+}O_y \longrightarrow CH_3^{\cdot} + M_x^{(n-1)}O_{y-1}(OH) \xrightarrow{O_2} M_x^{n+}O_y + HO_s$$

$$CH_3^{\cdot} + M_x^{n+}O_y \longrightarrow M_x^{(n-1)+}O_{y-1}(OCH_3) \longrightarrow M_x^{n+}O_y + CH_3O_s^{-} \longrightarrow \text{Diffusion into crystal (cr)}$$

$$CH_3O_{cr} \longrightarrow CH_2O + H_{cr}^{-},$$

$$CH_3O_{cr}^{-} + H_2O_{cr} \longrightarrow CH_3OH + HO_{cr}^{-},$$

$$M_x^{n+}O_y + H^{-} \longrightarrow M_x^{(n-1)+}O_{y-1}(O^{\cdot-}) + {}^1/_2 H_2,$$

$$M_x^{(n-1)+}O_{y-1}(O^{\cdot-}) + CH_4 \longrightarrow CH_3O_{ads}^{\cdot} + M_x^{(n-1)+}O_{y-2}(OH) \longrightarrow M_x^{n+}O + HO_s,$$

$$CH_3O_{ads}^{\cdot} + O_{ads}\ (\text{or } O_s) \longrightarrow CH_2O + HO_s,$$

$$CH_3O^{\cdot} + CH_4 \longrightarrow CH_3OH + CH_3^{\cdot},$$

$$CH_3O_{ads}^{\cdot} \xrightarrow{O_2} H_2O + CO \xrightarrow{Cat} CO_2,$$

$$HO_{s(cr)} + HO_{s(cr)} \longrightarrow H_2O + O_{s(cr)},$$

In the primary chemical event, hydrogen is abstracted from methane by the exceedingly mobile, bearing a high electron density, oxygen atom of the catalyst lattice. The resulting methyl radical $CH_3^{\cdot}$ further interacts with the lattice oxygen to give a methoxyl ion $CH_3O^{\cdot}$, which can, at the instant of regeneration of the reduced metallic centers of the catalyst by oxygen from the reaction mixture, penetrate into the crystal bulk (by virtue of the specific behavior of heteropoly acids with respect to polar species [134]), to be converted there to formaldehyde. Together with the main reactions, the species conversion in macrokinetic stages of the process is considered.

With some salts of heteropoly acids used, it is possible to raise the conversion of methane, yield of formaldehyde,

and throughput of the catalyst by factors of 2, 3, and 40, respectively, compared with the known results.

CONCLUSIONS

The material presented above suggests the following. The methane oxidation to formaldehyde has been extensively studied, with the systems MoO_3/SiO_2 and V_2O_5/SiO_2 examined to a considerably greater extent, compared with other catalysts. The yield of formaldehyde on these systems does not exceed 3–4%; higher yields have been reported for other catalysts, but, as a rule, this could not be confirmed by other researchers. This is presumably due to specific features of the experiment, disregarded by other researchers (stronger recirculation, rapid cooling after leaving the reactor), rather than to direct errors. However, even the yields actually achieved for the given process are practically important and economically justified.

A number of scientific schools adhere to the so-called heterogeneous-homogeneous oxidation mechanism and data disagreeing with this concept are not interpreted by these researchers whenever possible. This means that clear evidence that the lattice oxygen is involved in the process and formaldehyde is formed in some cases on the surface, rather than in the bulk of the gas phase, fails to receive due attention. There is no particular published evidence that formaldehyde can be formed outside the working zone of a catalyst, although it would by surely unreasonable to deny the possibility that the methyl radical may escape into the gas phase.

Further, numerous authors adhere to the purely radical reaction pathway, although their own data point to a high probability of the ion-radical pathway of the reaction on heterogeneous catalysts and, primarily, on ambivalent metals, which change the degree of oxidation of the central atom in the course of a catalytic cycle.

It also follows from the material presented that heteropoly acids are promising, but so far poorly studied, catalysts on which, in particular, the yield of formaldehyde can be markedly raised.

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