Translated from *Uspekhi Khimii* 61 2040–2061 (1992) U.D.C. 541.128.13

The partial catalytic oxidation of methane to give oxygen-containing compounds

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ABSTRACT. **The three principal paths of the partial oxidation of methane, to give methanol, formaldehyde, and synthesis gas, have been reviewed. The kinetics and mechanism of the processes have been described. The possible oxidation of methane using different oxidising agents—oxygen and carbon dioxide—has been examined.**

The bibliography contains 139 references.

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I. Introduction

Among the various routes in the partial oxdiation of methane, the recently discovered oxidative condensation of methane to give C_2-hydrocarbons is being most intensively developed. The number of publications on this topic is much greater than the number devoted to other possible routes for the partial oxidation. A number of recent reviews deal with the partial oxidation of CH_4.[1,2]

At the same time, the practical importance of the other directions is apparently much greater than that of oxidative condensation. Among these, the oxidation of methane to methanol occupies a leading position. Methanol is an important component of oxygenate fuels for internal combustion engines. The demand for methanol amounts to millions of tons in this country, and tens of millions of tons worldwide. Thus the search for new economical methods for obtaining methanol, making it possible to replace the traditional method of preparation via synthesis gas, has become one of the most important directions in catalytic studies.

Synthesis gas ($CO + H_2$) is usually obtained by the steam conversion of methane on a nickel catalyst at a high temperature (1000–1200 K)

$$CH_4 + H_2O = CO + 3H_2.$$

In this version, however, the mixture obtained cannot be used directly for the synthesis of methanol, since this requires a different stoichiometric ratio $[CO]:[H_2] = 1:2$. This can be obtained by the direct oxidation of methane using oxygen

$$2CH_4 + O_2 = 2CO + 4H_2.$$

The oxidative transformation of methane to synthesis gas with a ratio $[CO]:[H_2] = 1:1$ is achieved by using CO_2 as the oxidising agent

$$CH_4 + CO_2 = 2CO + 2H_2.$$

This mixture can be used to obtain hydrocarbons by the Fischer–Tropsch synthesis.

The third position of economic importance is occupied by the partial oxidation of methane to formaldehyde. The discovery of selective catalysts for the direct oxidation of methane to formaldehyde would make it possible to replace by a single-stage process the multi-stage methane → synthesis gas → methanol → formaldehyde process.

Reviews of the partial oxidation of methane to oxygen-containing compounds have been published.[3–6] The present review examines publications up to and including 1991 (and early 1992). The liquid-phase homogeneous-catalytic oxidation of methane is not examined.

II. The oxidation of methane to methanol

Homogeneous oxidation. The homogeneous oxidation of methane has been studied in most detail at 673–873 K. It takes place with the intermediate formation of the free radicals CH_3, CH_3O, CH_3O_2, HO_2, HCO, and OH and the molecular species H_2O_2 and CH_3OOH. The kinetics of the formation and disappearance of the free radicals under the conditions of the reaction are often determined by freezing the free radicals in a CO_2 matrix using a trap cooled with liquid nitrogen. The use of freezing in this way combined with ESR *in situ* was first developed in the Erevan Institute of Chemical Physics.[7] A detailed scheme for the oxidation of methane, describing the principal stages of the process, has been published.[8] The reactions

determining the overall rate of the process, and the corresponding rate constants, are given below:

$CH_4 + O_2 = CH_3 + HO_2$, $k_1 = 10^{-10}\exp(-230/RT)$, (1)

$CH_3 + O_2 = CH_3O_2$, $k_2 = 4 \cdot 10^{-13}$, (2)

$CH_3O_2 + M = CH_3 + O_2 + M$, $k_3 = 10^{-14}\exp(-109/RT)$, (3)

$CH_3O + O_2 = CH_2O + HO_2$, $k_4 = 5 \cdot 10^{-14}$, (4)

$OH + CH_4 = CH_3 + H_2O$, $k_5 = 10^{-10}\exp(-35.5/RT)$, (5)

$HO_2 + CH_4 = H_2O_2 + CH_3$, $k_6 = 10^{-12}\exp(-90/RT)$, (6)

$OH + CH_2O = HCO + H_2O$, $k_7 = 1.6 \cdot 10^{-10}\exp(-10.4/RT)$, (7)

$HO_2 + CH_2O = HCO + H_2O_2$, $k_8 = 1.9 \cdot 10^{-11}\exp(-54/RT)$, (8)

$HCO + O_2 = CO + HO_2$, $k_9 = 5.5 \cdot 10^{-11}$, (9)

$H_2O_2 + M = 2OH + M$, $k_{10} = 2.8 \cdot 10^{-7}\exp(-193/RT)$, (10)

$CH_3O_2 + CH_4 = CH_3OOH + CH_3$, $k_{11} = 10^{-12}\exp(-82/RT)$, (11)

$CH_3O_2 + CH_2O = CH_3OOH + HCO$, $k_{12} = 10^{-17}$, (12)

$CH_3OOH = CH_3O + OH$, $k_{13} = 4 \cdot 10^{-15}\exp(-179/RT)$, (13)

$CH_3O + CH_4 = CH_3OH + CH_3$, $k_{14} = 10^{-12.2}\exp(-46/RT)$, (14)

$OH + CO = CO_2 + H$, $k_{15} = 1.6 \cdot 10^{-12.5}\exp(-3.3/RT)$, (15)

$H + CH_2O = H_2 + HCO$, $k_{16} = 1.6 \cdot 10^{-10}\exp(-18/RT)$, (16)

$H + CH_4 = H_2 + CH_3$, $k_{17} = 5 \cdot 10^{-9}\exp(-49.7/RT)$, (17)

$HO_2 + HO_2 = H_2O_2 + O_2$, $k_{18} = 4 \cdot 10^{-12}$, (18)

$H_2O_2 = H_2O + \frac{1}{2}O_2$, $k_{19} = 0.1$, (19)

$OH + H_2O_2 = H_2O + HO_2$, $k_{20} = 1.7 \cdot 10^{-11}\exp(-7.5/RT)$, (20)

$HO_2 + CH_3OH = H_2O_2 + CH_2OH$ $k_{21} = 1.6 \cdot 10^{-12}\exp(-60.3/RT)$, (21)

$CH_3 + CH_3 = C_2H_6$, $k_{22} = 3 \cdot 10^{-11}$. (22)

The rate constants of the unimolecular, bimolecular, and termolecular reactions have the units s^{-1}, cm^3 $molecule^{-1}$ s^{-1}, and cm^6 $molecule^{-2}$ s^{-1} respectively, and the activation energy E_a has the units kJ mol^{-1}. According to this scheme, the chain reaction is initiated by reaction (1), and chain propagation takes place mainly by reactions (2)–(9), (11), (12), and (15)–(17). The main reaction responsible for chain branching is the decomposition of the hydroperoxide CH_3OOH (13), and additional chain branching takes place by the decomposition of H_2O_2 to OH radicals in reaction (10). The principal branching agent is formed by reaction (11) in the initial stages, and by reaction (12) in subsequent stages.

The formation of various products by the oxidation of methane has been examined in a number of studies.[9–15] Reactions (2) and (3) are the forward and back reactions of the equilibrium

$$CH_3 + O_2 \rightleftharpoons CH_3O_2. \quad (23)$$

Equilibrium (23) is displaced to the left at high temperatures and to the right at low temperatures: the heat of the reaction is $Q = -\Delta H \simeq E_a = 109$ kJ mol^{-1}. Thus CH_3 radicals play an important role in the oxidation of methane at higher temperatures. The role of most of the radical reactions increases with increase in temperature. Chain termination takes place by reactions (18) and (22), but mainly by the reactions of the radicals on the walls of the reactor.

Recent studies[9–11] have shown that if later data[16] are used, the value obtained for the equilibrium constant of reaction (23) is 200 times smaller. This leads to a decrease in the previously calculated concentrations of CH_3O_2 and to an increase in the concentration of CH_3 radicals. As pointed out in a number of papers on the oxidative condensation of methane,[1,2] CH_3O_2 radicals lead mainly to extensive oxidation, and CH_3 radicals lead to the oxidative condensation of methane, that is to reaction (22).

The probability of formation of methanol is greatest at high pressures and high ratios of the concentration $[CH_4]:[O_2]$. The main reaction leading to the appearance of CH_3OH is reaction (14). At high pressures (5–10 MPa), the relative role of the different stages changes. The yield of methanol increases significantly, and that of formaldehyde decreases. According to a detailed scheme for the oxidation of methanol,[9–11] a significant contribution to the overall mechanism under these conditions is made not only by reaction (14) but also by the reaction:

$CH_3O + H_2O_2 = CH_3OH + HO_2$, $k_{24} = 2.5 \cdot 10^{-13}\exp(-16.7/RT)$. (24)

The CH_3O radical is formed not only by reaction (13) but also by the reactions

$2CH_3O_2 = 2CH_3O + O_2$, $k_{25} = 1.7 \cdot 10^{-13}$, (25)

$CH_3O_2 + CH_3 = 2CH_3O$, $k_{26} = 4.5 \cdot 10^{-11}$. (26)

CH_3OH is consumed in reaction (21) and also in the reactions

$CH_3OH + CH_3O_2 = CH_3OOH + CH_2OH$, $k_{27} = 5 \cdot 10^{-3}\exp(-60/RT)$, (27)

$CH_3OH + HO_2 = CH_2OH + H_2O_2$, $k_{28} = 1.5 \cdot 10^{-12}\exp(-60/RT)$. (28)

Considering the products of extensive oxidation, CO is formed by reaction (9) and the reaction

$HCO + M = CO + H + M$, $k_{29} = 4 \cdot 10^{-10}\exp(-71/RT)$. (29)

The disappearance of CO and the formation of CO_2 take place by reaction (15) and the reactions

$HO_2 + CO = CO_2 + OH$, $k_{30} = 2.2 \cdot 10^{-10}\exp(-96/RT)$, (30)

$CH_3O + CO = CH_3 + CO_2$, $k_{31} = 2.6 \cdot 10^{-11}\exp(-49.4/RT)$, (31)

$CH_3O_2 + CO = CH_3O + CO_2$, $k_{32} = 1.7 \cdot 10^{-10}\exp(-100/RT)$. (32)

In the high-temperature extensive oxidation of methane the most important reactions are those of the H and O atoms and the OH radical, and not the radical CH_3, CH_3O_2, and CH_3O. The reaction of the radicals with the walls of the reactor is less significant at high pressures than at low pressures.

At 5–10 MPa and 673–873 K the theoretical yield of methanol may reach several percent, calculated for the methane passed. For this purpose, mixtures with very high ratios $[CH_4]:[O_2] = 30-100$ are used. At $[CH_4]:[O_2] = 50$, the yield of CH_3OH in a pilot plant is 1% and the selectivity ~50% for 100% conversion of oxygen.

The selectivity can be increased by finding appropriate conditions for the direct recombination of the radicals

$$CH_3 + OH = CH_3OH. \quad (33)$$

The yield of methanol can also be increased by adding hydrogen to the mixture to give the reactions

$$CH_3OO + H_2 = CH_3OOH + H, \quad k_{34} = 3.6 \cdot 10^{-12}\exp(-93.3/RT), \quad (34)$$

$$CH_3O + H_2 = CH_3OH + H, \quad k_{35} = 3.6 \cdot 10^{-12}\exp(-41.8/RT). \quad (35)$$

The economics of the homogeneous oxidation of methane to methanol have been examined. For example, it has been pointed out[5] that for 100% selectivity of the oxidation of CH_4 to CH_3OH the cost of methanol would be 172 dollars per ton, compared with 248 dollars per ton for the usual method of synthesis. In Russia this process may be even more favourable, since the cost of natural gas is relatively low.

Catalytic oxidation. A catalyst should not be expected to have a marked influence on the rate of the oxidation of methane to methanol at a high pressure. Nevertheless, studies of this topic appear from time to time. For example, catalysts based on the oxides of zinc, cadmium, and nickel have been added to a high-pressure reactor (10 MPa). An increase in selectivity from 50% to 80% was reported.[17,18] The results were not subsequently confirmed, however.

In studies[3,19,20] of the oxidation of CH_4 at a high pressure (3.5–12.5 MPa), 623–723 K, and $[CH_4]:[O_2] = 20:25$, a high selectivity with respect to methanol was achieved—75–80% compared with 40–50% reported by other authors. These experiments were carried out in a stainless steel reactor. This raises the question of the possible influence of the material of the reactor on the oxidation of CH_4 to CH_3OH. Treating a stainless steel reactor with alkali (KOH) decreased the yield of CH_3OH, but did not decrease the yield of CH_3OCH_3, also present in the reaction products; Ni and Cu lowered the yield of methanol considerably. A direct study[20] of heterogeneous and homogeneous additives showed that under these conditions the reactor material has relatively little influence on the reaction rate. The best heterogeneous additive was SnO_2, and the best homogeneous additive was 2,3-dimethylbutane. The results[19,20] showing an increase in selectivity in a stainless steel reactor are not consistent with other studies. For example, other authors[21] obtained a selectivity of only 40% under similar conditions.

The initiating action of a solid catalyst on the oxidation of CH_4 at a high pressure has also been studied.[22] A platinum wire at a temperature of 520 K was introduced at a distance of 10 cm before the reaction zone in a stainless steel reactor lined with quartz, at a pressure of 4.1 MPa, a component ratio $[CH_4]:[O_2]:[N_2] = 30:1:4$, and a reaction temperature of 653–779 K. The reaction temperature was lowered by 60 K. The selectivity with respect to CH_3OH was lowered slightly, but adding 4 mol% H_2 at 673 K produced an almost two-fold increase in the selectivity. The maximum selectivity at this temperature, however, was only 34.6%. In the opinion of the authors cited,[22] the key stage corresponds to reactions (34) and (35). Hydrogen on the surface possibly reacts more effectively than H_2 in the gas phase.

A theoretical analysis and experimental data obtained using M^+ and $(M=O)^+$ ion beams showed that the direct reaction of $(M=O)^+$ with CH_4 to give CH_3OH is possible for M = Fe or Os:

$$FeO^+ + CH_4 \longrightarrow Fe^+ + CH_3OH. \quad (36)$$

The Fe^+ ions obtained can be re-oxidised using N_2O.[23]

Fe=O groups may also be present on the surface of solid catalysts, and their reaction with CH_4 may lead to the direct formation of methanol [reaction (36)] or to the additional generation of CH_3 radicals

$$MO + RH \longrightarrow \dot{M}OH + \dot{R}, \quad (37)$$

which at an increased pressure lead finally to an increase in the yield of methanol.

On the basis of this idea, the firm Sun Oil developed a catalyst for oxidising CH_4 to methanol, consisting of sodium sodalite subjected to partial ion exchange with Fe^{II}.[24] In contrast to the homogeneous process, in this case a significant selectivity in the conversion of CH_4 into CH_3OH was obtained at $[CH_4]:[O_2]$ ratios which were not very high. At 700 K, 5.3 MPa, and $[CH_4]:[O_2] = 3:1$ the selectivity increased from 44% for the homogeneous process to 77% in the presence of Fe–Na-sodalite; the conversion of CH_4 increased from 4.8% to 6.5%. Silicoferrate gave a selectivity of 66% for 5.5% conversion at 688 K.[25] The most promising catalyst is sodium sodalite containing about 13% Fe, the acidity of which had been completely removed by previous reactioin with NaN_3. The authors of a patent[25] state that non-framework cationic iron hydroxo-centres are necessary in the catalyst. Dinuclear $Fe^{II}OFe^{II}$ centres are preferable to $Fe^{III}OFe^{III}$ centres, that is over-oxidation of iron poisons the catalyst.

Data have also been published on the use of acidic catalysts, in particular superacids, for the oxidation of methane to methanol. A selectivity with respect to CH_3OH of 77% (and even 100% with respect to $CH_3OH + CH_2O$) for 3.5% conversion was obtained on the superacid catalyst $Cr^{3+} - Zr^{4+}SO_4/SiO_2$ at a low temperature (523 K). The author cited[26] considers that the reaction involves the intermediate formation of the CH_5^+ ion. The selective formation of CH_3OH from CH_4 on zeolites at increased pressures has been reported: on H-ZSM-5 at 693 K [29] and on Cu-ZSM-5 at 613 K.[28] Oxidation using N_2O gives a higher selectivity than oxidation using O_2. Fe-ZSM-5 zeolite under the same conditions gives only CO and CO_2.[28]

The problem of developing oxidation catalysts for methanol has not been solved. Many studies are not being continued, and published results are not confirmed by subsequent studies. The most promising results have been obtained using Fe-containing catalysts at high pressures and relatively low temperatures. The most probable explanation is additional generation of CH_3 radicals and their subsequent reactions to give CH_3OH.

III. The oxidation of methane to formaldehyde

Homogeneous oxidation. Unlike methanol, formaldehyde is formed with a high probability at low pressures and low concentration ratios $[CH_4]:[O_2]$. It is formed by the decomposition of the hydroperoxide CH_3OOH in reaction (13) and then from the CH_3O radical in reaction (4). The hydroperoxide precursor of formaldehyde is formed mainly by reaction (11), that is from the CH_3O_2 radical.

Calculations[8] carried out for 738 K and initial concentrations $[CH_4] = 3.2 \times 10^{18}$ molecule cm^{-3} and $[O_2] = 10^{18}$ molecule cm^{-3} gave the following maximum values of the concentrations of intermediate products (particle cm^{-3}): $[HO_2] = 4.9 \times 10^{13}$, $[CH_3O_2] = 3.9 \times 10^{12}$, $[CH_3OOH] = 2 \times 10^{14}$, $[CH_3] = 4.7 \times 10^{12}$, $[CH_3OH] = 4 \times 10^{15}$, $[CH_2O] = 2 \times 10^{16}$, $[H_2O_2] = 8 \times 10^{15}$. According to these calculations, which on the whole agree with experimental data, the yield of the desired product of the partial oxidation, that is formaldehyde, is about 1% calculated for the methane reacting, and the yield of methanol is lower by a factor of about ten. The principal oxidation products are CO and CO_2. ~2% ethane is formed. Later calculations[10,11] altered these figures slightly, giving a higher yield of CH_2O and a lower yield of C_2H_6.

Formaldehyde is also formed by the reaction

$$2CH_3O_2 = CH_3OH + CH_2O + O_2, \qquad k_{38} = 7.4 \cdot 10^{-14}, \qquad (38)$$

and is consumed mainly in reactions (7) and (8).

According to a published scheme,[13] in a flow reactor at 773–873 K, the recombination of CH_3 radicals [reaction (22)] with the formation of C_2H_6 predominates at low volume rates, and the reaction

$$CH_3 + O_2 = CH_2O + OH, \qquad (39)$$

predominates at high volume rates.

The decomposition of CH_2O under homogeneous flow conditions has been studied.[14,21] At 873 K for 20% conversion of methane, about 60% CH_2O decomposes in the empty reactor. According to experimental data,[14] the maximum yield of CH_2O (3.46%) was obtained for a mixture with $[CH_4]:[air] = 1:5$ at 923 K and 5 MPa (6.7% conversion, selectivity 51.6%). Under these conditions, filling the reactor with SiO_2 and other oxides lowers the yield of formaldehyde.

Catalysts of the oxidation of methane to formaldehyde. Dowden and co-workers[29] were among the first to study the oxidative conversion of methane into formaldehyde. According to their theoretical ideas, a catalyst for the production of formaldehyde should have the functions of dehydrogenation and the introduction of an oxygen atom. Oxides of Fe^{3+} and Cr^{3+} are best for the first function, and oxides of V^{5+}, Mo^{6+}, Ti^{4+}, and Zn^{2+} are best for the second. Of the catalysts studied,[29] the oxides of Cr^{3+} and Mn^{3+} had the highest activity; Fe^{3+} phosphate had medium activity, but the highest selectivity.

A large number of oxide catalysts were subsequently studied. An appreciable activity in the formation of formaldehyde was shown by pure SiO_2 (finely divided quartz, or silica gel).[30–32] The low selectivity of Al_2O_3 [30,31] was attributed to the high rate of the successive conversion of formaldehyde to oxides of carbon both by oxidation and by the decomposition of CH_2O to $CO + H_2$. The yield of CH_2O on silica gel at 879 K was 2% (selectivity 34%, 6.1% conversion). Modifying the silca gel with B_2O_3 increased the yield to 3.5%. On an aluminosilicate modified by H_3PO_4 the yield of CH_2O was 2.9% (selectivity 48%, 6% conversion), and on an aluminosilicate modified by H_3BO_3 the yield was 2.5% (selectivity 3.5%, 7% conversion).

HCl increases both the total conversion of methane on SiO_2 and the yield of formaldehyde. According to Mel'tser and co-workers,[33] HCl poisons the centres responsible for the extensive oxidation of CH_2O to CO_2. Covering the SiO_2 with hydrogen peroxide also increases the yield of CH_2O.[34]

A large number of oxides, phosphates, and silicates have been studied as catalysts of the oxidation of methane to formaldehyde.[35–37] In the opinion of the authors cited, a high selectivity and a high yield can be obtained on catalysts with a high acidity. High yields of CH_2O were obtained, for example, at 873 K on tin phosphate $Sn_2P_2O_7$ (9.0%, selectivity 96%), on SiP_2O_7 (5.1%, selectivity 82.8%), and on an aluminosilicate treated with H_3PO_4. It was also shown that the best of the transition metal phosphates are those most difficult to reduce. It is considered[35] that on the acidic OH groups the following reaction takes place:

$$CH_4 + {-OH_s} \longrightarrow {-OCH_3} + H_2O \xrightarrow{O_2} \begin{matrix} -O \\ \diagdown \\ \quad CH_2 \\ \diagup \\ -O \end{matrix} \longrightarrow$$

$$\longrightarrow CH_2O + O_s(-OH_s).$$

Under recirculating conditions with freezing of the products, the yield of formaldehyde reached 14–16%, and even 18% in some experiments.

Aluminosilicates containing 10–11% Al_2O_3 and modified by added oxides of iron, zirconium, vanadium, cerium, bismuth, and chromium have also been studied;[38–40] the yield of CH_2O was ~2%. The maximum yield (2.6%) was obtained on an aluminosilicate containing added 2% cerium phosphate and 0.05% P_2O_5 at 1023 K. Adding 0.2–0.5% dimethyl ether $(CH_3)_2O$ to the content zone made it possible to lower the reaction temperature by 100 K and to raise the yield of CH_2O to 5–5.6%.[40] It is possible, however, that a significant contribution to the yield of formaldehyde is made by the decomposition of dimethyl ether itself. The use of circulation of the reaction mixture with the removal of both CO and CO_2 from the mixture made it possible to increase the yield of CH_2O to 12.5% and the selectivity to 65% on one of the most active catalysts, $Mo-P-Al-SiO_2$.[39]

Almost all workers who have studied the oxidation of methane to formaldehyde have used SiO_2 or aluminosilicates as carriers. MgO and Al_2O_3 were more active than SiO_2, but gave only CO and CO_2.

Various oxides deposited on SiO_2 to concentrations of 9.2% have been studied on catalysts.[42] The highest yields of CH_2O at 923 K and $[CH_4]:[O_2] = 1$ were obtained on Ga_2O_3 (3.6%), Bi_2O_3, Al_2O_3, and ZrO_2, and the highest selectivity on P_2O_5, WO_3, B_2O_3 (>60%), Sb_2O_3, Nb_2O_5, Al_2O_3, and MgO (>30%). Here also, the acidic oxides are more active.

The largest number of studies has been carried out for the MoO_3/SiO_2 system.[42–50] On this catalyst, CH_4 is oxidised to CH_2O at 823–923 K. 85% selectivity was achieved for ~3% conversion, and 30% selectivity for 7% conversion. Formaldehyde is not formed on pure MoO_3 without SiO_2. The selectivity was increased by adding oxides of chromium[44] and copper,[46] but adding iron, chromium, cobalt, and sodium[47] lowered the selectivity of CH_2O formation compared with Mo/SiO_2, although some of them increased the degree of conversion. The catalyst $CoMoO/SiO_2$ at 873 K gave a selectivity of 50.3% for the oxidation of CH_4 to CH_3OH, and of 16.9% for the oxidation to CH_2O.[44] A system consisting of the deposited complex $MoCl_5/R_4Sn/SiO_2$ has also been studied[50] as starting material for the synthesis of a catalyst. The process was based on the ease of the replacement of the M=O group in the ligand by the carbene complex $M=CH_2$, which it is assumed could be converted directly into CH_2O. A selectivity of 80% was obtained for a low degree of conversion.[50]

A significant increase in the yield of oxygen-containing products on MoO_3/SiO_2 was achieved using N_2O instead of O_2 as oxidising

agent.[46,51–58] At 823 K the degree of conversion of CH_4 on a 1.7% MoO_3/SiO_2 catalyst increased from 0.5% to 6.0%, and the selectivity reached 55% for CH_2O and 38% for CH_3OH.[54] The highest yield of CH_2O and CH_3OH was obtained by adding water vapour to the original mixture; at P_{H_2O} = 20 kPa the total selectivity with respect to CH_3OH + CH_2O reaches 99% for 26% conversion. Other authors[56,57] also reported a high selectivity of the oxidation of CH_4 to CH_2O using N_2O, but with a much lower degree of conversion. The activation energy of this reaction is ~170 kJ mol^{-1}.[58]

At a concentration of 1–5% Mo in SiO_2, molybdosilicic acid is formed on the surface and takes part in the oxidation of methane to formaldehyde.[56] Appreciable selectivity in the oxidation of CH_4 by N_2O (up to 80% for 2% conversion) was observed[59–65] on heteropolyacids $HPMo_{12}O_{40}$ and their salts, deposited on SiO_2. A correlation between the acidity of the heteropolyacid and the yield of CH_2O has been reported.[66] A very high yield of CH_2 (12–16%) was obtained.[66] Breakdown of the Keggin structure at a temperature above 873 K leads to the loss of activity and selectivity. The activity of $H_3PMo_{12}O_{40}/SiO_2$ increased in the presence of chlorine-containing additives such as CH_2Cl_2 or CCl_4; at 799 K the degree of conversion was 12%, and the selectivity 32%.[65]

A mixed catalyst containing oxides of molybdenum, iron, bismuth, nickel, and magnesium deposited on SiO_2 showed a selectivity of 86.5% in the oxidation of CH_4 to CH_2O for 8.9% conversion at 923 K.[67]

V_2O_5/SiO_2 gave results similar to those for MoO_3/SiO_2.[49] In the oxidation of CH_4 to formaldehyde using N_2O, a 2% V_2O_5/SiO_2 catalyst gave appreciable activity at temperatures 80–100 K lower than those for MoO_3/SiO_2.[53,57] The activation energy was 88 kJ mol^{-1}. The possibility of increasing the selectivity on membrane V_2O_5/SiO_2 catalysts has been reported.[68] For 1% conversion, the selectivity with respect to CH_2O increased from 5% to 20%.

Unusual effects in both of the reactions CH_4 + O_2 and CH_4 + N_2O were detected in a study of the influence of mechanochemical activation on the catalytic properties of the systems MoO_x/SiO_2, VO_x/SiO_2, and WO_x/SiO_2.[69–72] After mechanical mixtures of Mo + SiO_2, MoO_3 + SiO_2, V + SiO_2, and V_2O_5 + SiO_2 has been ground in a ball mill or subjected to high pressure with shear in a Bridgman cell, practically no extensive oxidation was observed. The selectivity with respect to formaldehyde increased to 100% for 3% conversion at 873 K. At the same time, MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts impregnated before grinding showed no change in selectivity even after grinding; a change was observed only after the mechanical grinding of a mixture of the two oxides. Electron microscopy and electron diffraction showed that under the conditions of the mechanical treatment of a mixture of the two oxides, encapsulation takes place, that is the particles of the active phases MoO_3 or V_2O_5 are covered with silica gel. This encapsulation is confirmed by a study of the Mössbauer spectra of mixtures of Fe and SiO_2 powders subjected to mechanical grinding. Encapsulated iron, covered with silica gel, remains in the metallic state under the conditions of CH_4 oxidation, whereas ordinary iron powder is oxidised to Fe_2O_3 under these conditions.

The encapsulation of the oxides of molybdenum or vanadium in SiO_2 capsules alters the fractions of the active centres involved in the partial and extensive oxidation of methane. The centres of CO_2 formation are blocked, but the CH_2O formation centres remain. The enveloping of M_xO_y by silica gel also apparently hinders the supply of electrons to the molecule being oxidised. The oxidation of CH_4 to CH_2O requires only half the number of electrons required to oxidise CH_4 to CO_2.

Active phases have also been deposited on SnO_2. On Bi_2O_3/SnO_2, methane is oxidised by oxygen with a selectivity with respect to CH_2O of ~80%. In the reaction of CH_4 with N_2O on the same catalyst, the selectivity with respect to CH_2O reaches 98.2% for 2.6% conversion.[73] Formaldehyde is also formed on an MoO_3 monolayer deposited on SnO_2.[74]

Fe-containing catalysts (like Mo-containing catalysts) have often been used to convert methane into formaldehyde.

Fe–Nb–B–O is a selective catalyst.[73] At a fairly high temperature (1023–1073 K), 70–80% selectivity was obtained for 2.7–14.3% conversion and a yield of CH_2O of 2–3.8%. The activation energy of the process is 250 kJ mol^{-1}. X-Ray photoelectron spectroscopy (XPS) detected the phases $FeNbO_4$, $FeNb_{11}O_{29}$, Fe–Nb–B–O (oxidation state of iron > 3+), and B_2O_3 on the surface. Oxidation using N_2O on the same catalyst gave the same selectivity and the same activation energy, but the activity was halved. A published study[76] of the activity of various oxides in the oxidation of methane to formaldehyde to some extent represents a continuation of other work.[75]

A high selectivity has been obtained on $MoO_3.Fe_2O_3$.[77] The same authors reported[78] a very high yield of CH_2O (22.5%) and a selectivity of 83.6% on this catalyst, but no subsequent work has been published. On $Fe_3(PO_4)_2$ promoted using $La_3(PO_4)_2$, a selectivity with respect to CH_2O or 30% was observed for 3.7% conversion at 953 K.[79] Water vapour lowered the selectivity of the transformation of CH_4 into CH_2O, as a result of the formation of HCOOH. At the same time, on pure Fe_2O_3, only extensive oxidation was observed. Adding 1% CuO and 1% Fe_2O_3 to ZnO gave the catalyst $Cu_{0.01}Fe_{0.01}Zn_{0.98}O$, which showed a selectivity of 43% for 0.02% conversion at 823 K, and a selectivity of 10% for 2.5% conversion at 1023 K.[80] XPS indicated the presence of Cu^+ and Fe^{3+} on the surface of this catalyst. Its activity and selectivity were much higher than on pure ZnO. The authors cited[80] attribute its behaviour in the oxidation of CH_4 to CH_2O to the necessity of a combination of redox properties (Fe^{2+}/Fe^{3+} and Cu^+/Cu^{2+}) and Lewis acidity (Fe^{3+}).

The results of a number of studies of iron-containing catalysts have been analysed.[14] It was concluded that the highest yields of CH_2O on these catalysts are no higher than those obtained under the same conditions in an empty reactor.

Data have also been published on metallic catalysts of the oxidation of methane to formaldehyde. According to Wang and co-workers,[81] palladium promoted with CH_2Cl_2 can bring about the selective oxidation of methane to formaldehyde. It has been shown,[14] however, that at 723–873 K only extensive oxidation is observed on Pd modified by chlorine. An increase in the selectivity of the action of anatase was observed after it was modified with CH_2Cl_2; a yield of CH_2O of 2.8% was obtained at 848 K.

The selective oxidation of methane by another oxidising agent (CO_2) was carried out on brass gauze with a specific surface of 24.3 m^2 g^{-1} which had been oxidised and reduced several times. When CH_4 + CO_2 pulses are introduced into a stream of nitrogen at 653–733 K, the only oxidation product is formaldehyde. If however methane is added to CO_2 as carrier gas, only methanol is obtained, in yields of 1.23–4.36% at 873 K.[82]

It is difficult to identify general regularities in the selection of catalysts of the oxidation of methanol to formaldehyde. Nevertheless, in the work of most authors, three groups of catalyst are clearly distinguished: 1, Mo- or V-containing deposited oxide catalysts; 2, Fe-containing oxide catalysts; 3, acidic catasyts. Despite the relationship between selectivity and acidity noted by

various workers, oxide systems deposited on SiO_2 were more active and selective than oxides deposited on Al_2O_3 or aluminosilicates.

In almost all cases the oxidation of methane to formaldehyde was carried out at temperatures 100–200 K lower than the oxidation condensation of methane, that is at 723–973 K. As in the oxidative condensation of methane, various limiting yields apparently exist; their values (3–4%) are appreciably lower than those in the oxidative condensation of methane. The individual cases where higher yields were obtained[35,40,66,77] require further study.

Mechanism of the catalytic oxidation of methane to formaldehyde. Two mechanisms of the oxidation of methane to formaldehyde are distinguished: 1, a heterogeneous–homogeneous mechanism, in which the selectivity is controlled mainly by gaseous reactions; 2, a heterogeneous mechanism, in which the selectivity is controlled by processes on the surface. The existence of limiting yields tends to support the heterogeneous–homogeneous mechanism. On the other hand, data on the chemical features of the selection of catalysts tend to support the heterogeneous mechanism. The mechanism of the oxidation of methane to formaldehyde is examined in a large number of publications.

The detection of free radicals under the conditions of the oxidation of methane to formaldehyde provides the principal evidence for the heterogeneous–homogeneous mechanism. One of the first studies proving the formation of CH_3O_2 radicals in this reaction involved freezing out the radicals in a CO_2 matrix.[30] According to the scheme given by the authors cited, however, an increase in the yield of free radicals facilitates non-selective extensive oxidation and leads to a decrease in the yield of CH_2O.

Adding C_2H_6 to a $CH_4 + O_2$ mixture increased the selectivity of the oxidation of CH_4 at 833–913 K to CH_2O on SiO_2 and decreased the yield of CO. This was attributed[83] to an increase in the formation of methyl radicals from C_2H_6. Under the given conditions, CH_3 radicals are converted into CH_3O_2 and CH_3O. A correlation has been noted[33] between the yield of CH_3O_2 radicals and the yield of CH_2O under the conditions of the oxidation of methane on SiO_2. With increase in temperature, the yield of CH_2O and the concentration of RO_2 pass through a maximum at 903 K. HCl increases the total degree of conversion, but decreases the yield of radicals, although the yield of CH_2O increases. According to the authors cited,[33] HCl poisons the centres for the extensive oxidation of CH_2O to CO_2. Depositing H_2O_2 on SiO_2 also increases the yield of CH_2O and free radicals.[34]

According to Otsuka and co-workers,[75] on an Fe–Nb–NB–O catalyst, methyl radicals are formed in the primary reaction of methane with the surface oxygen O_s, and formaldehyde is formed by the secondary reaction of CH_3 with O_s;

$$\begin{aligned} &CH_4 + O_s \longrightarrow CH_3 + OH_s, \\ &CH_3 + O_s \longrightarrow CH_2O + \tfrac{1}{2} H_2, \\ &2OH_s \longrightarrow O_s + H_2O. \end{aligned} \qquad (40)$$

It is considered[84] that the selectivity of action of catalysts of the oxidative condensation of methane can be displaced from C_2-hydrocarbons to CH_2O by changing the conditions of the process. Increase in the flow rate of a mixture with $[CH_4]:[O_2]:[Ar] = 6:1:6$ over an MgO catalyst from 1000 h^{-1} to 48 000 h^{-1} increased sharply the selectivity of the oxidation of CH_4 to CH_2O. For 9% conversion of O_2, a selectivity with respect to CH_2O of 65% was observed, but at 11% conversion of O_2 the selectivity decreased to almost zero, with a simultaneous increase in the selectivity of the transformation to CO to 65% and the appearance of ethane. With increase in the conversion the selectivity with respect to C_2H_4 and CO_2 increases. Following the scheme given by Gesser and co-workers,[19] Hargreaves and co-workers[84] examined the competition between two main reactions: the recombination of CH_3 radicals [reaction (22)] and their oxidation to CH_2O [reaction (39)]. The first reaction is kinetically of second order with respect to CH_3, and its probability is higher at low flow rates, whereas the second is of first order with respect to CH_3, and its probability is greater at high flow rates. At low pressures in the gas phase, CH_3 radicals are converted into CH_3OH.

Thus according to Hargreaves and co-workers,[84] the same catasts increase the rates of both the oxidative condensation of methane and the oxidation of CH_4 to formaldehyde and methanol. The part played by the catalyst involves the generation of CH_3 radicals, and the selectivity is determined by secondary gas-phase reactions.

The same conclusion, namely that CH_2O can be obtained at high volume rates of a $CH_4 + O_2$ mixture, was reached by other workers.[85] Under these conditions, a selectivity of 28% was obtained for the oxidation of methanol to CH_2O on silica gel at 873 K, for 12% conversion. It has been shown[76] that ethane and formaldehyde have as precursor the same intermediate product, apparently the CH_3 radical, and that the direction of the reaction is determined by the external parameters, mainly temperature and pressure.

The nature of the primary centres O_s in the catalyst, activating methane, is also important. Isotopic exchange experiments[75] showed that the oxygen of the catalyst O_s is firmly bound and does not exchange with $^{18}O_2$ under the catalysis conditions. It is lattice oxygen, and not oxygen from the gas phase, that is mainly introduced into the reaction products CH_2O, CO, and CO_2.

Additional data on the nature of the centres O_s are obtained by studying the catalysts by ESR. MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts show ready reduction of the $\equiv Mo^{VI}=O$ and $\equiv V^{V}=O$ groups to the radical centres $Mo^{VI}O^-$ and $V^{V}O^-$ respectively and then to $Mo^{V}O^-$ (or $Mo^{V}OH^-$) or $V^{IV}O^-$ (or $V^{IV}OH^-$). The centres O^- detected by ESR are readily formed by the reaction of these catalysts with N_2O

$$Mo^{V} + N_2O \longrightarrow Mo^{VI}O^- + N_2. \qquad (41)$$

A mechanism has been proposed[51,52] for the subsequent reaction of CH_4 with these centres:

$$\begin{aligned} &Mo^{VI}O^- + CH_4 \longrightarrow Mo^{VI}OH^- + CH_3, \\ &Mo^{VI}O^{2-} + CH_3 \longrightarrow Mo^{V}OCH_3. \end{aligned} \qquad (42)$$

Decomposition of the surface methoxyl groups gives formaldehyde

$$Mo^{V}OCH_3^- + Mo^{VI}O^{2-} \longrightarrow Mo^{V}OH^- + CH_2O, \qquad (43)$$

and their reaction with water gives methanol

$$Mo^{V}OCH_3^- + H_2O \longrightarrow Mo^{V}OH^- + CH_3OH. \qquad (44)$$

Non-selective oxidation takes place by the reaction

$$8Mo^{VI} + 4O^{2-} + CH_4 \longrightarrow 8Mo^{V} + 2H_2O + CO_2, \qquad (45)$$

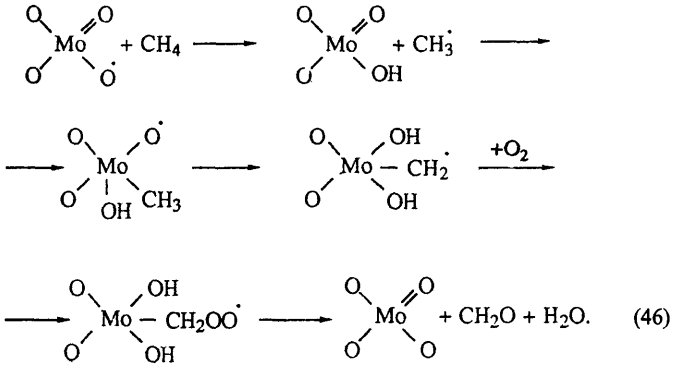
that is one-electron transfer from the centres O^- gives CH_2O, and two-electron transfer from the centres O^{2-} gives CO_2. According to this scheme there are no homogeneous stages, apart from the generation of free radicals and their reaction on the surface.

Methoxyl groups have been detected from their infrared spectra on Mo/SiO_2 and V/SiO_2 catalysts.[51,52,86,87] It has also been pointed out that on other catalysts, OCH_3 groups may be intermediate

products in the extensive oxidation of methane.[88] In contrast to the case of methane, in the oxidation of CH_3OH the activity and selectivity were lower when N_2O was used as oxidising agent than when O_2 was used.[89] O^- evidently does not take part in the oxidation of metanol.

V_2O_5/SiO_2 is one of the few catalysts in which the formation and disappearance of stabilised O^- on reduction and oxidation have been conclusively established by ESR.[90] O^- is formed by the reaction of N_2O with $V^{4+}O/SiO_2$. The reaction of O_2 with this catalyst gives O^- and O_2^-.[91]

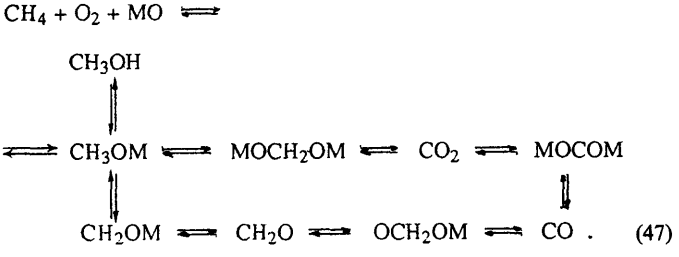
The mechanochemical grinding of $MoO_3 + SiO_2$ gives high concentrations of Mo^{5+} radical centres. The following mechanism was proposed for the oxidation of CH_4 on this catalyst:[72]



(46)

Pure SiO_2 without molybdenum or vanadium shows a fairly high selectivity with respect to CH_2O (up to 38%), but a low activity at 873 K.[92] Heating SiO_2 to 1273 K increases both the yield of CH_2O and the selectivity (to 53%). The high-temperature dehydroxylation of SiO_2 apparently leads to the formation of radical and biradical centres on the surface.

Purely heterogeneous schemes for the oxidation of methane to formaldehyde have also been published. For example, the oxidation of CH_4 on deposited MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts has been modelled[50] using the rate constants, selected from the literature, of the surface stages of the parallel–consecutive scheme (only the principal steps are given):



(47)

On the whole, the scheme provides a satisfactory description of the experimental data. Here, the explanation for the limiting yields of formaldehyde is that it is an intermediate product in the oxidation to CO. The oxidation of CH_4 to CH_3OH takes place in parallel, and CO_2 is formed by two paths: directly from methane via surface transformations, and with the intermediate formation of CO in the gas phase.

Nevertheless, there are more data in support of the heterogeneous–homogeneous mechanism. The following conclusions have been established.

1. The active centre are stabilised radical centres on the surface of the oxides, probably O^-.

2. The reaction of methane with them gives CH_3 radicals, which escape into the gas phase.

3. At a temperature below 879–929 K they react with oxygen, forming CH_3O_2, CH_3O, and CH_3OOH, which finally give formaldehyde.

4. At high temperatures, long contact times, and high pressures, transformations of the radicals give other products: CO, CO_2, C_2H_6, C_2H_4, decreasing the selectivity with respect to formaldehyde.

The mechanism of the formation of CH_2O on acidic catalysts is less clear. In this case also, possibly, latent homolytic stages should be sought.

Experimental modelling of the oxidation of methane to formaldehyde. Controlled conditions can be used to establish the part played by various parameters in catalysis. Such conditions can be created photochemically and mechanochemically.

The influence of γ-irradiation on a V/SiO_2 catalyst in a $CH_4 + O_2$ mixture has been studied.[93] Subsequent thermal desorption led to the formation of up to 15% formaldehyde. In the opinion of the authors cited,[93] the most probable source of CH_2O is surface methoxyl groups formed by the reaction

$$CH_3 + O^- \longrightarrow CH_3O^-,$$

although methoxyl groups were not detected on the surface. The formation of CH_2O was also observed on ultraviolet irradiation of 5% MoO_3/SiO_2 in a mixture with $[CH_4]:[O_2] = 3:1$ at 473 K.[94] CO and CO_2 are formed at a higher temperature.

When TiO_2 [95] and MoO_3 [96] are irradiated in $CH_4 + O_2$ mixtures, small quantities of methanol are formed.

The molybdenyl bond in MoO_3 can be activated both photochemically and by thermal excitation[97–99] by the reaction

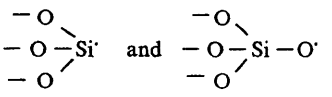
$$Mo^{VI}O^{2-} \rightleftharpoons [Mo^{V}O^{-}]^*.$$

The $Mo^{V}O^-$ pairs were not detected by ESR, because of their short lifetime, but were detected by photoluminescence. The reaction of the O^- in this pair with CH_4 can give CH_3 radicals.[100]

The phototransformations of $CH_4 + O_2$ on various oxides have been studied.[101] Two competing processes were observed: the formation of hydrocarbons and oxygen-containing products. Excitation by light in the band gap leads mainly to the formation of oxygen-containing products, and excitation of the impurity levels to the formation of hydrocarbons. The dissociative photo-adsorption of CH_4 leads to the formation of excited surface OH groups. The surface is gradually poisoned, but can be regenerated by high-temperature treatment in oxygen.

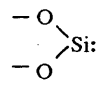
The study of the oxidation of methane by ESR *in situ* is made difficult by the very low concentration of active centres. In addition, they are situated on the surface of the oxide catalyst. This makes it impossible to study them in the presence of such gases as O_2 or H_2O. High concentrations of free-radical centres can be obtained by mechanical treatment, for example by grinding the oxides in a ball mill.

The mechanical grinding of SiO_2 gives very high concentrations of defects:[102–107] $10^{12}-10^{13}$ cm^{-2}, that is up to 1% of the number of surface atoms. Free-radical defects are formed by the homolytic splitting of siloxane bonds

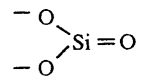


Grinding in oxygen also leads to the formation of $\equiv Si-O-O^{\cdot}$ and

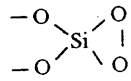
$\equiv Si-O-O-O^{\cdot}$ centres. The silicon atom is joined to three lattice oxygen atoms. A second type of defect is diamagnetic; the Si atom is joined to two O atoms of the lattice. In this set, silicone groups



silanone groups



and siladioxirane groups



have been identified. The reactions and transformations of these groups in contact with methane and oxygen have been studied.

The radical centres $\equiv Si-O^{\cdot}$ react with methane to give CH_3 radicals

$$\equiv Si-O^{\cdot} + CH_4 \longrightarrow \equiv Si-OH + CH_3. \quad (48)$$

The reaction takes place rapidly even at 78 K without significant activation energy. The CH_3 radicals are subsequently captured by diamagnetic centres; the structure of the new formations has been determined by ESR.

$$=Si: + CH_3^{\cdot} \longrightarrow =\dot{S}i-CH_3,$$

$$=Si= O + CH_3^{\cdot} \longrightarrow =Si\begin{matrix}O^{\cdot}\\ \diagdown CH_3\end{matrix} \longrightarrow =Si\begin{matrix}OH\\ \diagdown CH_2^{\cdot}\end{matrix},$$

$$=Si\begin{matrix}O\\ \diagdown O\end{matrix} + CH_3^{\cdot} \longrightarrow =Si\begin{matrix}O^{\cdot}\\ \diagdown OCH_3\end{matrix} \longrightarrow =Si\begin{matrix}OH\\ \diagdown OCH_2^{\cdot}\end{matrix} \quad (49)$$

Despite the high concentration of radical centres $=Si-O^{\cdot}$, practically no reaction between them and CH_3 is observed. The reaction of oxygen with the centres formed by reaction (49) gives formaldehyde

$$\equiv Si-CH_2^{\cdot} + O_2 \longrightarrow \equiv Si-CH_2OO^{\cdot} \longrightarrow \equiv Si-O^{\cdot} + CH_2O,$$

$$\equiv Si-OCH_2^{\cdot} + O_2 \longrightarrow \equiv Si-OCH_2OO^{\cdot} \longrightarrow \equiv Si-O-O^{\cdot} + CH_2O. \quad (50)$$

To complete the catalytic cycle, it is necessary to add to reactions (48)–(50) another stage, namely the dehydration of the $\equiv Si-OH$ group. This is apparently the most difficult stage.

Another possible route for the formation of CH_2O is by the thermal decomposition of the methoxyl groups, which on SiO_2 takes place at 973 K [108,109]

$$\equiv Si-O-CH_3 \longrightarrow \equiv Si-H + CH_2O. \quad (51)$$

The formation of methoxyl groups was noted in the reaction of SiO_2 with methane.[108]

Thus the mechanochemical modelling of the oxidation of CH_4 on SiO_2 shows a similarity in the homogeneous and heterogeneous radical processes. The reaction of the molecules with the radical centres of the surface takes place readily; the regeneration of the active centres is difficult.

Formaldehyde can also be obtained by the reaction of free radicals, for example CH_3O_2, with the surface. The following reaction is probable on mechanochemically treated (MoO_3 + SiO_2)-catalysts

$$CH_3O_2 + Mo^{V}OH^{-} \longrightarrow CH_2O + H_2O + Mo^{V}O^{-} (\rightleftharpoons Mo^{VI}O^{2-}).$$

This reaction explains the experimentally observed formation of CH_2O at 823–879 K,[72] when the rate of the initial formation of CH_3 radicals is fairly high, but equilibrium (23) is displaced towards CH_3O_2.

IV. The oxidation of methane to synthesis gas

The oxidation of methane by oxygen. The oxidation of methane to synthesis gas is a weakly exothermic reaction

$$CH_4 + {}^1/_2O_2 = CO + 2H_2, \ \Delta H = -44 \text{ kJ mol}^{-1}. \quad (52)$$

Reaction (52) is thermodynamically allowed ($\Delta G < 0$) over a wide temperature range, and in principle can take place with a selectivity of 100%. This process is carried out non-catalytically, for example in the synthesis gas generators of Shell and Texaco in the range 1400–1700 K.[110,11]

On catalysts, reaction (52) is usually complicated by the extensive oxidation of methane

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (53)$$

and by the endothermic steam conversion of methane and reaction of CH_4 with CO_2

$$CH_4 + H_2O = CO + 3H_2, \ \Delta H = 207 \text{ kJ mol}^{-1}, \quad (54)$$

$$CH_4 + CO_2 = 2CO + 2H_2, \ \Delta H = 246 \text{ kJ mol}^{-1}. \quad (55)$$

Reaction (54) is displaced towards synthesis gas above 580 K, and reaction (55) above 910 K. Conversion of water gas also takes place

$$CO + H_2O = CO_2 + H_2, \ \Delta H = -35 \text{ kJ mol}^{-1}. \quad (56)$$

The value of ΔG for reaction (56) at 1100 K is negative (−25 kJ mol^{-1} at 300 K); above 1100 K the equilibrium is displaced to the left.

Deposited nickel catalysts of the steam conversion of methane are most frequently used. In a flow reactor with a nickel catalyst deposited on a refractory material, different reactions were observed in different layers of the catalyst at 1002–1173 K.[112] The exothermic extensive reaction (53) took place in the first layer, and the endothermic reactions (54) and (55) in subsequent layers. This gave a CH_4 + CO + CO_2 + H_2 mixture, corresponding to thermodynamic predictions. Different reactions taking place in different layers have been observed in other studies.[110,113,114] Stoichiometric synthesis gas was obtained in CH_4 + O_2 mixtures with an oxygen deficit on nickel deposited on mullite.[113]

The activity and selectivity of nickel catalysts deposited on various carriers: Al_2O_3, $SiO_2-Al_2O_3$, $ZrO_2-Al_2O_3$, and HY zeolite, were studied.[110] 5% Ni on a carrier in all cases gave a selectivity with respect to CO_2 + H_2 > 90% and >92.5% conversion of CH_4; for Ni/Al_2O_3 and Ni/SiO_2-ZrO_2, a selectivity and conversion of about 96% were obtained. For 1% Ni, however, appreciable activity and selectivity were obtained only on the non-acidic carriers Al_2O_3 and SiO_2-ZrO_2. It was shown[110] that nickel cations on acidic carriers are not completely reduced to metal. Non-reduced nickel gives

practically no H_2 in the reaction products. All the catalysts were active and selective at high Ni concentrations (> 5%).

The oxidation of methane to synthesis gas on 25% Ni/Al_2O_3 at 723–1173 K was studied.[114] Above 973 K the selectivity with respect to CO + H_2 reaches 95% with complete conversion of CH_4. XPS and electron diffraction studies of the catalyst showed that in the first layer of the catalyst in the reaction mixture the spinel $NiAl_2O_4$, moderately active in extensive oxidation, is formed. In the second layer, a mixture of phases NiO + Al_2O_3, which is an active catalyst of extensive oxidation, is formed. In the third layer, reactions (54)–(56) take place as far as complete thermodynamic equilibrium. Thus it was confirmed that the oxidation of CH_4 to synthesis gas takes place by the sequence of reactions (53)–(56). This combination of reactions helps to overcome the highly endothermic character of the steam conversion of methane, that is reaction (54).

A combination of the steam and oxygen conversion of methane [reactions (54) and (52)] is carried out in industry. Steam conversion is carried out in the first reactor at 973 K and $[H_2O]:[CH_4] = 2$, and oxygen conversion in the second reactor at a low CH_4 concentration and 1223 K. This gives stoichiometric synthesis gas with a lower consumption of natural gas and energy.[115]

A study of the selective oxidation of methane to CO + H_2 on palladium catalysis deposited on oxides showed[116] that the catalysts 1% Pd(γ-Al_2O_3, Y_2O_3, La_2O_3, TiO_2, ZrO_2, HfO_2, CeO_2) give synthesis gas with a selectivity greater than 90%; for Pd/SiO_2 the selectivity at 1023 K was 63.7%. The degree of conversion of CH_4 at 1023 K was 35–66%. The highest selectivity (99.5%) was obtained on Pd/γ-Al_2O_3 for 58% conversion. The selectivity is lowered by the formation of CO_2, which in the opinion of the authors cited[116] takes place in the gas phase, while CO is formed on the surface.

The oxidation of methane at 673–973 K by noble-metal catalysts deposited on γ-Al_2O_3 has been studied.[117] In a reducing medium (a gas mixture with $[CH_4]:[CO]:[O_2] = 2:1:3$) a CO + H_2 mixture was obtained, and in an oxidising medium ($[CH_4]:[CO]:[O_2] = 2:1:10$) only extensive oxidation took place. The order of activity in the oxidation of CH_4 to synthesis gas is Rh > Pd $\simeq$ Pt. Adding CeO_2 to the catalyst suppresses completely its ability to give CO. CO in the gas phase has little influence on the yield of products.

Rh/SiO_2 was the most active and selective of the noble metals deposited on SiO_2.[118] On Rh, Ru, Pd, and Ni deposited on SiO_2, the yield of synthesis gas exceeded 90%. At the same time, extensive oxidation of CH_4 took place on Fe and Co/SiO_2. Oxidised metallic catalysts have a low activity.

Synthesis gas can be obtained by oxidising methane on catalysts containing lanthanides and noble metals, even at a low temperature (777 K).[119–121] On $Ln_2M_2O_7$ catalysts, where Ln = La, Eu, Gd, Yb, and M = Ru, Ir, a yield of CO + H_2 of 92–94% was obtained with a selectivity of up to 99% at a high volume rate of 4×10^4 h^{-1}. The highest selectivity (98–99%) was observed for $Y_2Ru_2O_7$. The catalysts Ru, Pd, Ir, Ni/Al_2O_3 were also active. X-Ray data showed that under the synthesis conditions the oxide catalyst decomposes to the metal

$$2Eu_2Ir_2O_7 \longrightarrow 2Eu_2O_3 + 4Ir + 4O_2.$$

Iridium particles with dimensions of 3 nm are formed. Reaction (56) decreases the selectivity slightly. The yield of CO + H_2 decreases with increase in pressure.

Thus the highest activity and selectivity in the oxidative conversion of methane into synthesis gas are shown by the metals of the platinum group and nickel, which activate hydrogen (and correspondingly the recombination of H atoms). This ability is lost when the metals are oxidised. After the removal of the first H atom, CH_4 is apparently transformed rapidly into $CH_{2\,ads}$, CH_{ads}, C_{ads}, and then CO. The process is undoubtedly highly selective, but its practical realisation requires the special production of oxygen, and this makes the large-scale production of synthesis gas by reaction (52) less favourable than steam conversion (54).

The combination of the oxidative conversion of CH_4 into synthesis gas with other reactions is also of interest. A combination of three reactors without intermediate separation has been used[122] for the selective oxidation of methane to propanal C_2H_5CHO. The oxidative condensation of methane to ethane on $K/BaCO_3$ and the transformation of $CH_4 + O_2$ into synthesis gas on 1% Rh/Al_2O_3 at a high temperature (1139–1153 K) are carried out in two parallel reactors. The hydroformylation of ethane on a homogeneous Rh catalyst is carried out in a third reactor at a low temperature (993 K). A selectivity with respect to C_2H_5CHO of 27% is achieved for 49% conversion.

The oxidation of methane using CO_2. The direct reaction of methane with CO_2 on metallic catalysts has been studied by many workers, beginning with the work of Fischer and Tropsch.[123] In addition to reaction (55), reactions (56) and (57) also take place. The formation of ethane [reaction (58)] is also possible:[124]

$$CH_4 + 2CO_2 = C + 2CO + 2H_2O, \quad (57)$$

$$CH_4 + 3CO_2 = 4CO + 2H_2O, \quad (58)$$

$$2CH_4 + CO_2 = C_2H_6 + CO + H_2O. \quad (59)$$

All four reactions (55) and (57)–(59) are endothermic and take place at high temperatures (900–1200 K). At 1073 K, $\Delta G < 0$ for reactions (55)–(58), and $\Delta G > 0$ for reaction (59).

Reaction (55) often takes place as a side reaction in the steam conversion of methane. A study of its kinetics on an Ni catalyst at 1070–1173 K showed[125] that the reaction rate is described by the same equation as the steam conversion

$$r = \frac{k_1 p_{CH_4}}{1 + k_2 p_{H_2O}/p_{H_2} + k_3 p_{CO}}, \quad (60)$$

where k_1, k_2, k_3 are constants, and p_{CH_4}, p_{H_2O}, p_{H_2}, and p_{CO} the partial pressures of methane, water, hydrogen, and carbon monoxide respectively. The explanation given[124] is that CH_4 reacts first not with CO_2 but with H_2O, and the hydrogen formed reacts rapidly with CO_2 by a reaction which is the reverse of reaction (56), with the regeneration of H_2O.

In accordance with Eqn. (57), the reaction of CH_4 with CO_2 gives carbon, which poisons the nickel catalyst. It is obtained both from methane by its dissociation to C + $2H_2$ and from CO by the Boudouard reaction. Various methods are used for the industrial preparation of synthesis gas from $CH_4 + CO_2$. The first of Haldor Topsoe uses a $CH_4 + CO_2 + H_2O$ mixture to decrease the poisoning of the catalyst and blocking of the tubes by carbon.[126,127] It has also developed the SPARG process (1173 K, 0.9 MPa), in which sulphur vapour is added to the reacting gases. Sulphur passivates nickel and prevents the formation of carbon.

Ni/SiO_2 was much more active than the oxides CaO and Fe_2O_3. The temperature of 50% conversion was 910 K on Ni/SiO_2, and 1200–1300 K on the oxides.[128] The oxides are covered by carbon more rapidly than nickel. At 1073 K the degree of conversion of a $CH_4 + CO_2$ mixture into synthesis gas was 83.1% on Ni/Al_2O_3,

74.2% on Co/Al_2O_3, and only 3.4% on Fe/Al_2O_3. The reaction rate was approximately 1.5 times lower on Ni/SiO_2 than on Ni/Al_2O_3.[129]

Metals of the platinum group are also active in the carbon dioxide conversion of methane.[130–133] The reaction takes place at an appreciable rate even at 773 K. A study of the reaction by the transverse pulse method showed that CO is formed when the CO_2 pulse is introduced. C_2H_6 and C_2H_4 are formed from the first CH_4 pulses, followed by rapid deactivation at 773 K and by slow deactivation at 823 K. Rh/Al_2O_3 and Pd/Al_2O_3 are poisoned more slowly than the others, and Ru/Al_2O_3 more rapidly. The order of specific activities in the $CO_2 + CH_4$ reaction is Rh > Pd > Ru > Pt > Ir/Al_2O_3, which corresponds to the order of the activities in the dissociation $CO_2 \rightarrow CO + O_{ads}$.[131] According to much of the data,[130,131,133] Rh/Al_2O_3 is the most active. Acidic carriers were found to be more favourable, since they facilitate the dispersion of the deposited metals.

The reversible reaction $CO_2 + CH_4 \rightleftarrows 2H_2 + 2CO$, that is the production of synthesis gas at high temperatures and methanation at low temperatures, is convenient for the creation of cells using solar energy;[132] the endothermic reaction takes place on heating by the sun, and the exothermic reaction takes place to remove the energy. The 1% Ru/Eu_2O_3 catalyst with a ruthenium particle size of 3 nm and the hexagonal ruthenium structure was found to be best for this purpose.

All the deposited noble metals studied were shown to be highly active.[134,135] Another important feature is that in almost all cases the product is a gas mixture with $[CO]:[H_2] = 1$, that is practically no side reactions take place. For a mixture with $[CH_4]:[CO_2] = 1$ at 1050 K, the yields of synthesis gas CO + H_2 were 1% on Al_2O_3, 85% on 1% Ni/Al_2O_3, 73% on 1% Pd/Al_2O_3, 89% on 1% Ru/Al_2O_3, 87% on 1% Rh/Al_2O_3, and 89% on 1% Ir/Al_2O_3. Coking was most rapid for the catalyst Ni/Al_2O_3 and Pd/Al_2O_3. The most stable to coking was Ir/Al_2O_3, which remained active for 260 h. On Ru/Al_2O_3 the yields of H_2 was greater than that of CO. In a $13CH_4 + 6O_2 + CO_2$ mixture the yield on Ni/Al_2O_3 can be increased by 91%, and the reaction becomes thermally neutral. For a $4CH_4 + O_2 + 9CO_2$ mixture the gas obtained contained exactly 50% CO and 50% H_2, and no carbon was formed on the surface.

New types of catalyst, stable to carbon formation, have been studied.[136–139] The effect of various additives on Ni/SiO_2 catalysts was studied. Of the oxides of nickel, iron, copper, chromium, and manganese, the oxides of manganese were found to be most effective. In their presence the extent of carbon formation decreased, and the degree of transformation of CO_2 increased with increase in the proportion of manganese in the nickel catalyst.

Subsequent study showed that reaction (55) can be carried out without nickel. A 5% Ca–12% Mn–O/Al_2O_3 catalyst was most effective under stationary conditions. In its presence at 1140 K at a volume rate of 900 h^{-1} with an equimolar mixture of CO and H_2, the conversion of CH_4 was 83.1%, the conversion of CO_2 62.7%, and the selectivity with respect to H_2 76.5%. At 1200 K at the start of work with a fresh catalyst, extensive oxidation of methane takes place involving the oxygen of the catalyst, and there is no transformation of CO_2. As the reaction and reduction of the catalyst take place, CO_2 is activated. The concentration of CO and H_2 increase continuously. With a catalyst operating under stationary conditions at 1200 K, the conversion of CO_2 and CH_4 is complete, and the selectivity is 99.7% for CO, and 84.6% for H_2. The activity is preserved for a long time, and practically no formation of carbon by reaction (57) takes place.

A study of the phase composition of an operating Ca–MnO/SiO_2 catalyst showed[137,138] that during the reaction the more highly oxidised phases Mn_2O_3 and Mn_3O_4 are reduced, and only the reduced phase MnO is detected in the catalyst. After the production of a stable catalyst composition, the formation of carbide and metallic manganese phases was not observed.

A study of the reaction under alternating conditions (the reaction of alternately CH_4 and CO_2 with the catalyst) showed that on the fresh catalyst, C_2H_4 and C_2H_6 are formed from methane, possibly with the participation of carbonate phases, since oxidative dimerisation takes place.[139] After reduction and phase transformation from the oxidised phases to MnO, the formation of C_2H_6 and C_2H_4 decreases and CO appears. The rates of formation of hydrogen under stationary catalysis conditions (3×10^{-3} mol g^{-1} h^{-1}) and in the reductive reaction of CH_4 with the catalyst (1.7×10^{-3} mol g^{-1} h^{-1}) are comparable. The rate of the reaction of CO_2 with the reduced catalyst (re-oxidation of the catalyst), however, is greater than the rate of reduction.

Mamedov[136] concluded that the conversion of methane to synthesis gas using CO_2 on a manganese catalyst does not take place by a redox mechanism. During the catalysis, the stationary phase MnO is not reduced and is not oxidised, but prevents carbon formation. Electron microscopy detected coke deposits as thin layers on the reduced MnO centres. CO_2 reacts with MnO and forms an intermediate carbonate complex on the surface, methane dissociates, and the carbon fragment reacts with oxygen.

$$CH_4 + MnO \rightleftarrows MnO \ldots C + 2H_2,$$
$$CO_2 + MnO \rightleftarrows MnCO_3,$$
$$MnCO_3 + MnO \ldots C \longrightarrow 2MnO + 2CO,$$
$$MnCO_3 + H_2 \longrightarrow MnO + CO + H_2O,$$
$$MnO \ldots C + H_2O \longrightarrow MnO + CO + H_2.$$

When redox additives are introduced into MnO, the reaction becomes an alternating redox reaction. Only reaction (58) is observed on a K–Cr–Mn–O/SiO_2 catalyst.

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Received 13th July 1992