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Oxidative conversion of methane

V S Arutyunov, O V Krylov

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Abstract. The data on various aspects of oxidative conversion of methane published in 1998 – 2004 are considered. The bibliography includes 295 references.

I. Introduction

The advent of the 21st century brought about radical changes in the views on the future prospects of the world power engineering and the role of various sources of hydrocarbon raw materials. It has become evident that the oil era is not everlasting and its decline is not far off.[1] It is small-power energetics that make use of alternative renewable energy sources, solar energy in particular. The power flux densities are still so low that they cannot, in principle, meet the rapidly growing demands of the world economy despite the declaratory statements on the developments in this field. Renewable bioresources are obviously inadequate to satisfy the demands of the population inhabiting our planet for food or to solve the problems of the world energetics. As for thermonuclear energy, it has virtually not been called into being yet and according to the most optimistic prognoses will hardly become a reality before the end of this century. Atomic energy introduces well-known problems and causes alarm in view of environmental safety, but will hardly have a reasonable alternative within the next few decades. This all means that, till the end of this century, mankind will have to rely mainly upon fossil fuel, *viz*., carbon and natural gas. In this context, their efficient exploitation and development of novel resource-saving and environmentally friendly technologies are of paramount importance. Considerable efforts should be given to further improvement of chemical processes for the conversion of gaseous and solid hydrocarbon raw material into more convenient types of energy carriers and promising chemical products.

Today, the crucial role of natural gas and gas-chemical processes in the economy of the 21st century and the fact that they will gradually replace the existing oil stock and petrochemical technologies are not in doubt. The recent 7th Natural Gas Conversion Symposium (NGCS7), the largest international meeting devoted to the problems of reforming of natural gas and light hydrocarbons,[2,3] has demonstrated a real breakthrough in the technology and commercialisation of chemical conversion of natural gas. In the three years elapsed from the previous Symposium, the leading world companies have brought into operation several large-scale pilot plants and started the realisation of several jumbo projects. The overall output of liquid products is expected to amount to 2×10^6 barrels per day with an overall gas consumption of about 166×10^9 m^3 per year. There are more than 20 large oil and gas producers all over the world continuously patenting their developments; the total number of patents in different aspects of 'gas-to-liquid' (GTL) technologies has reached 8000.[4] Several hundred reports on the use of catalysis in natural gas reforming presented at the 13th International Congress on Catalysis are evidence of high scientific activity in this field.

The main recent trend has become the intention of leading chemical companies to broaden the range of natural gas conversion products other than motor fuels. For example, the market of such products can be expanded owing to the greater manufacture of polymers, which has been implemented by several companies.

The world capital of gas-chemical technologies is now moving to Qatar. Recently, the state-owned company Qatar Petroleum completed agreements with the largest oil-and-gas producing and developing companies (Sasol, Chevron, ConocoPhillips, Shell, ExxsonMobil, *etc*.) to the total sum of USD $\sim 23 \times 10^9$, which corresponds to daily liquid product output of $\sim 700\,000$ barrels. This means that the total investment in the infrastructure of the gas industry of this small country will amount to USD $\sim 60 \times 10^9$. Considerable activity in the establishment of new gas-chemical enterprises is shown by Iran and other Middle Eastern countries as well as by Nigeria, Australia, Trinidad, *etc*. Unfortunately, Russian gas- and oil-producing companies still continue to direct their exclusive efforts to the export of raw materials despite the fact that for Russia, the world leader in the resources and production of natural gas, its reforming is of strategic importance. So far, not a single oil- or gas producing company or a representative of a state-owned or academic institution within Russia has shown interest in the work of the NGCS7. However, Russian scientists will hardly be able to carry out research at a really high level in this technologically complicated area that requires expensive modern equipment without financial support from large companies.

The specific nature of the domestic gas industry determines the need for financial support of fundamental research. The bulk of Russian natural gas is extracted from the gas fields of Urengoi and Yamburg, regions that are difficult of access, with inclement climate where the use of the existing foreign technologies is unprofitable or impracticable. In addition, Russia possesses substantial reserves in the form of nearly 600 marginal or low-

V S Arutyunov, O V Krylov N N Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, 119991 Moscow, Russian Federation. Fax (7-495) 651 21 91, tel. (7-495) 939 72 87, e-mail: arutyunov@center.chph.ras.ru (V S Arutyunov), tel. (7-495) 939 71 68 (O V Krylov)

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pressure gas fields that are hitherto unexplored due to the lack of efficient technologies for their transportation or reforming.

The results of investigations carried out by Foster Wheeler Energy Ltd. by request of Sasol[5] and those reported at the NGCS6[6] suggest that an enterprise on natural gas oxidative conversion and Fischer—Tropsch synthesis with a productive capacity of 30 000 barrels per day (1 400 000 tons per year) located in seaside regions in order to ensure easy sea transportation of the final products, costs capital outlays per unit of USD 25 000 per barrel of the daily product, *i.e.*, about USD 530 per ton per year. According to technical-and-economic assessments,[7] the investment cost for the construction of a gas-converting plant in the vicinity of the gas fields of the Yamal Peninsula exceeds USD 4×10^9 with a provisional pay-back period of $\sim$20 years, which makes such projects unacceptable *a priori*.

All of the current chemical productions and works-in-project (WIP) are based on the preliminary conversion of natural gas, which contains methane as the main component, into synthesis gas which represents a mixture of carbon monoxide and hydrogen. This technologically complicated energy-consuming process takes up from 50% to 75% of the total cost of the basic chemical products prepared from natural gas (ammonia, methanol, GTL-products, *etc.*), which is the reason for their high prime cost and high capital intensity. Even an insignificant reduction of the cost of synthesis gas significantly reduces the production costs of the final products. Therefore, the main goal of the studies on methane reforming is both the reduction of the cost price of the synthesis gas, which can also be achieved with the use of oxidative conversion, and development of new in principle approaches to oxidative conversion of methane irrelevant to the production of synthesis gas.

The number of publications devoted to different aspects of oxidative conversion of methane is increasing annually. However, in this review only the investigations carried out in the past 6–7 years are reviewed, since the literature data on this subject published before 1998 were considered in detail in the monograph[8] and earlier papers.

II. Oxidative conversion of methane into synthesis gas and hydrogen

Recently, the interest in hydrogen fuels has increased substantially, particularly with regard to its possible utilisation in vehicles.[9] Although about 97% of motor fuels are currently oil reforming products, it is expected that by the end of the next decade hydrogen will be extensively used as a fuel for the most popular production cars. Hydrogen will be used as an additive to organic fuels, as a fuel itself for internal combusion engines and as a power supply for fuel cells. The main hydrogen source is synthesis gas ($CO + H_2$).

There exist three methods for preparing synthesis gas:

1) steam reforming of methane (SRM)

$$CH_4 + H_2O \longrightarrow CO + 3H_2 + 226 \text{ kJ mol}^{-1};$$

2) partial oxidation of methane (POM)

$$CH_4 + \frac{1}{2}O_2 \longrightarrow CO + 2H_2 - 44 \text{ kJ mol}^{-1};$$

3) carbon-dioxide ('dry') reforming of methane (CDR).

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 + 261 \text{ kJ mol}^{-1}.$$

Only the first of these reactions is widely employed in the large-scale production of nearly 95% of synthesis gas. A Shell plant in Bintoulou (Malaysia) that makes use of non-catalytic POM is an exception. Different modifications are reported that represent combinations of the above reactions. Irrespective of the process used to prepare synthesis gas, further elucidation of the reaction mechanism, the choice of effective and stable catalysts and efficient technological design still remain the topical tasks.

1. Steam reforming of methane

Since the introduction, in 1966, of SRM over nickel catalysts into industrial practice, a systematic solution of a wide range of problems related to sulfur poisoning of catalysts, coke formation and reduction of reactor size has begun. The SPARG technology developed by Haldor Topsoe Ltd. allowed solution of the problem of sulfur poisoning by reducing the overall catalyst activity and using a preconverter. Supported nickel and cobalt catalysts promoted by basic oxides possessed the highest activities. At present, the activity of a catalyst is not a limiting factor in SRM and the main efforts are focused on improving heat- and mass-exchange, optimisation of the process and minimisation of the reactor size.

The theoretical aspects of SRM were considered by Rostrup-Nielsen *et al.*[10–12] Steam reforming is accompanied by carbonisation of nickel catalysts, since carbon fibres appear upon decomposition of methane; their growth results in destruction of the catalyst, prevents interaction of the gas flow with the surface and impairs heat exchange.

A simplified scheme of this process was developed based on the concept of ensembles on surfaces of metals.[13]

$$CH_4 + Ni \longrightarrow Ni-CH_x \longrightarrow Ni_m-C \longrightarrow$$
$$\longrightarrow [C,Ni] \longrightarrow \text{filamentous C},$$
$$Ni_n-CH_x + Ni-OH_y \longrightarrow Ni + CO + H_2,$$
$$Ni_m-C + Ni-OH_y \longrightarrow Ni + CO + H_2$$

($m > n$).

The state and reactivity of the surface carbon are the key problems in the mechanism of SRM. The adsorbed carbon atoms do not react with gas molecules and are dissolved in Ni to generate carbon filaments that block the catalyst surface. A carbon-free mode is reached where the concentration of dissolved carbon [C, Ni] is below the equilibrium concentration of carbon. This ratio can be achieved by increasing the steam-to-carbon ratio and, correspondingly, adsorption of water vapour and the rate of the surface reaction with a simultaneous decrease in the rate and degree of activation and dissociation of CH_4.

The Topsoe company is the world leader in both the development of technologies for the production of synthesis gas and the use of the newest physical methods for the study of the reaction mechanism. Electron microscopic *in situ* studies on a specially designed instrument with the atomic resolution[14] enabled detailed investigations into the mechanism of methane activation over Ni. CH_4 molecules interact with the steps of Ni nanocrystals to form graphite-like clusters, which were further transformed into multilayered carbon nanotubes. Growth of the nanotube occurs in parallel with the rearrangement of the nickel particles which changes their shapes and sizes. After complete encapsulation of Ni, the growth of the nanotube stops and the catalyst is poisoned. Synthesis gas is formed in the reaction of the CH_x groups with the OH groups formed upon H_2O adsorption. A scheme was proposed that explained the promoting effect of MgO, La_2O_3, Ce_2O_3 and alkalis favouring adsorption of water. Total adsorption of H_2O over Ni/Al_2O_3 or $Ni/MgAl_2O_4$ exceeded that over Ni/MgO where a larger amount of the OH groups is formed as followed from the data on the isotope exchange with D_2O.[14] This accounts for the little coke formation over MgO. In this case, the amount of the OH groups increased despite a decrease in the dissociation rate of CH_4 by more than an order of magnitude. Over Co, the value of x in the CH_x groups was larger than over Ni, and over Ni/MgO it was larger than over Ni/SiO_2.

The mechanism of SRM was studied at the level of elementary reactions[15] using Ni single crystals as surface catalysts. The data obtained were consistent with the results of quantum-chemical calculations obtained by the DFT (Density Functional Theory) method. A comparison of reactions occurring on the plain surface of Ni(111) single crystal and on the step-like surface of Ni(211)

revealed that in the latter case the values of the activation energies in all the stages of the sequence:

$$CH_4 \longrightarrow CH_3 \longrightarrow CH_2 \longrightarrow CH \longrightarrow C \longrightarrow CO$$

were smaller than on the plain surface, although the corresponding values for different stages of this sequence were different. The SRM reaction was structure-sensitive: the facet of Ni(111) was catalytically active in SRM, but was inactive in carbon deposition. In contrast, both the catalytic reaction and carbon deposition occurred on the facet of Ni(211). On the whole, the presence of steps and other structural defects is unfavourable for SRM.

It was found that the degree of methane conversion was low at low metal-to-carbon binding energies.[16] The optimum energies of the M–C and metal-to-hydrogen (M–H) bonds are equal to 160–169 and 64–67 kcal mol^{-1}, respectively, which have been recommended as criteria for the selection of promoters for Ni catalysts.

a. Catalysts

As usual, supported nickel catalysts are mainly employed in SRM. The improvements applied largely to the shape of the pellets. Some newly developed catalysts have the shape of complex rings with multiple holes. Heat transfer on the walls of the reactor tubes is often a limiting factor in SRM, therefore, application of a thin layer of a catalyst directly onto the reactor walls is beneficial.

A highly active catalyst for SRM at a low $H_2O:CH_4$ ratio was prepared from perovskite $LaNi_xFe_{1-x}O_3$ ($0 < x < 1$).[17] At 800 °C, the selectivity towards CO reached 96%. In the majority of catalytically active systems ($0.2 < x < 0.4$), perovskite $LaFeO_3$ and finely dispersed Ni particles are formed under the conditions of SRM. Carbon deposition was the lowest over catalysts with this composition.

$CaAl_2O_4$ was found to be a good support for Ni and Rh catalysts.[18] The equilibrium conversion over $Ni/CaAl_2O_4$ and $Rh/CaAl_2O_4$ was reached at 400 °C and 480 °C, respectively, the volumetric gas flow rate being 10-fold larger than in conventional industrial reactors.

b. Kinetics and mechanism

Removal of hydrogen or CO from the reaction zone favours a shift of the equilibrium in SRM to the right and thus favours the increase in the yields of the target products. Metal membranes can be used to remove hydrogen,[19,20] which also reduces the risk of poisoning of the catalyst with hydrogen sulfide present in methane. Removal of CO_2 from the reaction zone can be carried out by binding it with an adsorbent, *e.g.*, CaO.[21]

$$CH_4 + 2H_2O + CaO \longrightarrow 4H_2 + CaCO_3.$$

In this case, regeneration of the adsorbent, *i.e.*, decomposition of $CaCO_3$, is required. A gas containing more than 95% of dry H_2 can be prepared in one step. After 25 cycles, the activity of the adsorbent decreased insignificantly.

Extensive studies into SRM are currently underway at the Institute of Catalysis of the Siberian Branch of the RAS. It was found[22] that the reaction rate decreased with the increase in the amount of the catalyst (Ru/Al_2O_3 or Ni/Al_2O_3), which is believed to support a hypothesis on a homogeneous–heterogeneous mechanism of this reaction. The maximum activity of Ni/Al_2O_3 corresponds to the activity of a wire of metallic nickel. At higher content of the catalyst, the reaction is purely heterogeneous (800 °C). The introduction of hydrogen decreases the activation energy and increases the rate of carbon formation.

The application of a thick layer of a catalyst ($Ni/Al_2O_3/Al$) onto the surface of a tubular reactor for SRM facilitates heat exchange on the tube walls.[23] A tubular heat-exchange reactor for SRM has been considered[24] where deep oxidation of methane took place on the outer surface coated with Ni–Cr-foam over perovskite, while steam reforming occurred on the inner surface of the Ni-foam catalyst. A combination of exothermic and endothermic reactions separated by the reactor wall enables a design of a virtually thermoneutral reactor.

The kinetics of SRM over a $Ni/\alpha\text{-}Al_2O_3$ catalyst were studied.[20] The reaction rate was proportional to the partial pressure of hydrogen p_{H_2}. The surface interaction $CH_{4\,ads} + H_2O_{ads}$ is the limiting step of this reaction, which occurs according to the Langmuir–Hinshelwood mechanism. As noted previously,[20] the first study[25] devoted to the steam reforming of CO had been published nine years before the frequently cited paper.[26]

c. Technological features

The start-up of a BP large pilot plant in Alaska constructed according to an original technology was a prominent event in the history of SRM technologies. Its daily capacity is 300 barrels of liquid GTL products at a production cost of USD 86×10^6. The SRM process enables the reduction of the prime cost of synthesis gas by excluding expensive oxygen. It was claimed[2] that it was possible to design a much more compact SRM apparatus with the mass smaller by 75% than that of analogous units.

Microchannel Process Technology (MPT) developed by Velocys Inc. is a novel promising approach to the study of SRM, since it substantially intensifies heat and mass exchange. A typical MPT reactor consists of stacks of closely spaced thin plates that form microchannels with diameter < 1 mm. The stacks where heat carrier is circulating or fuel is combusted alternate with those where reforming of natural gas occurs, which is accompanied by absorption of heat. A nearly 100-fold increase in the heat exchange intensity in comparison with conventional SRM processes made it possible to reduce significantly the overall dimensions of the equipment and to diminish the residence time. The latter circumstance is especially important for steam reforming, since soot formation takes much more time than the reforming itself. Very fast (< 10 ms) attainment of equilibrium concentrations in MPT reactors makes it possible to avoid soot formation, to increase the productivity and to reduce production costs. The trials conducted for several months demonstrated the durability of the MPT reformer. With this design, higher capacity is achieved by merely multiplying the number of stacks; no scaling-up is required. The operation principle of the MPT reactor is applicable to the subsequent steps of reprocessing of synthesis gas, *viz.*, the Fischer–Tropsch synthesis or synthesis of methanol.[27]

Despite the intensive search for alternative methods for methane conversion into synthesis gas and the appearance and ever increasing number of production technologies based on them, the SRM reaction is still the main industrial method for the production of synthesis gas. Although this reaction is highly endothermic, it is considered to be a candidate of choice as a hydrogen source in hydrogen technology. Steam reforming of methane is a high-tech process ensuring lower prime cost of H_2 in comparison with its production from biomass or using nuclear, solar and electric energy or wind power.

2. Partial oxidation of methane (POM)

Despite the indisputable achievements in the practical application of SRM, partial oxidation and combined steam-oxygen reforming of methane are the most popular trends of research. In addition to minimisation of power input, these methods allow production of synthesis gas with the composition ($H_2:CO = 2:1$), which is especially favourable for the Fischer–Tropsch synthesis and synthesis of methanol. The main problems include the necessity of using expensive oxygen, high explosion hazard and local overheating. Besides, the large size of POM reactors is a considerable obstacle to their commercialisation. Continuous search for novel technologies for oxidative conversion of methane into synthesis gas is underway.

A gas-phase method for the oxidation of methane to synthesis gas is being developed in Russia. This approach is based on the use of modified diesel or compression engines that also serve as the chemical reactors.[28,29] The process first implemented on a large

scale in 1998 is characterised by much higher overall productivity of the process per unit volume (10 000 m^3 of the synthesis gas per hour). The possible use of low-pressure natural gas (including that obtained from gas wells that can no longer be exploited for commercial purposes) and coal mine methane and oxidation by atmospheric air are its obvious advantages. However, the synthesis gas thus produced contains ~60% of nitrogen, which impedes its further processing. At the same time, simultaneous generation of electric energy is a very attractive feature of this process, although future prospects for its wide application are still ambiguous.[30]

Synthesis gas generators based on rocket technologies is yet another achievement of Russian scientists in the field of oxidative conversion of methane. The productivity of this process per unit volume exceeds those of conventional large-scale units by a factor of tens. Both processes are based on the gas-phase oxidation of methane at high temperatures and yield mixtures with nearly equilibrium composition. However, the composition of the synthesis gas is difficult to control by reason of high specific capacity of such units.[30] A pilot plant for motor fuels with a productivity of 432 kg h^{-1} with respect to methane has been constructed on the basis of a synthesis gas generator using rocket technologies.[31] Nevertheless, the Shell plant at Bintulu (Malaysia) is the only example of a successful industrial application of a gas-phase high-temperature (1100–1200 °C) POM process. Apparently, the POM technology will further be developed in connection with agreements on the construction of a supergiant plant at Qatar with the participation of the Shell Corporation.[32]

a. Catalysts

As a rule, the POM technology employs supported nickel [33–39] or, less frequently, cobalt [40] catalysts or catalysts based on precious metals.[41–46] Most of the studies in this field are aimed at increasing the stability of Ni over various oxide supports and the resistance of the catalyst against carbon poisoning rather than at enhancing its activity and selectivity. Studies of supported Ni catalysts revealed that Ni/CeO_2 and Ni/TiO_2 were much less active and selective in comparison with Ni/ZrO_2 and Ni/Al_2O_3, but less prone to carbon poisoning.[33] Nickel catalysts supported onto perovskites $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$ by solid-phase crystallisation were less active and less stable than those prepared by impregnation.[34,35] High dispersity of Ni prevents coke formation. $Ni/SrTiO_3$ possessed the highest dispersity. High stability and activity were observed for $Ni/CeO_2–ZrO_2$.

Promotion of $Ni/\gamma\text{-}Al_2O_3$ with Li and La oxides increased its stability and suppressed sintering, which results in a loss of activity.[36,37] $LiLaNiO/\gamma\text{-}Al_2O_3$ not only manifested high activity and high resistance to carbon deposition, but also possessed a stable porous crystalline structure, which remained unchanged even after 500-hr heating at 800 °C. The activity and stability of the nickel catalyst were considerably enhanced upon promotion with CeO_2 or Y_2O_3.[38,39] Cerium dioxide suppressed the interaction of Ni with Al_2O_3 and the growth of Ni crystals, and the latter remain as small particles. Carbon deposition decreased, while the stability of the catalyst increased.

Among a variety of supports for cobalt catalysts, only MgO proved to be suitable.[40] Following calcination at 800 °C, 24% Co/MgO possessed stable and high activity. The results of X-ray phase analysis suggest that only solid solutions of $Co_xMg_{1-x}O$ formed at $T > 800$ °C, while heating at $T < 800$ °C yielded Co_3O_4 and $MgCo_2O_4$.

Catalysts based on the platinum group metals, rhodium in particular, possess high activities and selectivities. Studies of Rh-catalysts have shown [41] that easily reducible supports, such as CeO_2, Nb_2O_5, Ta_2O_5, MnO_2, UO_2, did not enable as high stability and selectivity as non-reducible supports did, *e.g.*, MgO, $\gamma\text{-}Al_2O_3$, La_2O_3, Y_2O_3 and SiO_2. Rh/MgO was the catalyst of choice. Presumably,[41,42] its high stability is attributed to the strong interaction of Rh with MgO. The ease of formation of transient compounds in the course of preparation of the supported Rh-catalysts decreased in the following order: $MgRh_2O_4 > LaRhO_3 > YRhO_3 > RhTaO_4$.[44] The catalysts Rh/MgO and Rh/La_2O_3 retained their activities and selectivities for 100 h at 750 °C, while Rh/Y_2O_3 and Rh/Ta_2O_5 rapidly deactivated under these conditions, but were active at higher temperatures (900 °C). The stability and selectivity of Rh/Al_2O_3 increased with an increase in the concentration of rhodium.[46] Rhodium catalysts supported onto hexaaluminates $BaAl_{12}O_{19}$, $SrAl_{12}O_{19}$ and $CaAl_{12}O_{19}$ were both active and selective, but less stable than $Rh/\alpha\text{-}Al_2O_3$. Composite La–Co–Ni-perovskites containing 5% Rh supported on a honeycomb corundum monolith with channels 1 mm in diameter manifested high activity and stability.[47] At 850 °C, carbon deposition on these catalysts was negligibly small.

Bimetallic catalysts $Pt–Co/\alpha\text{-}Al_2O_3$ manifested higher selectivity in the reaction $CO + H_2$ than their monometallic platinum analogue;[48] in addition, no coke formation occurred on their surface for 80 h. According to X-ray phase analysis data, Pt and Co phases were formed under the conditions of the catalytic reaction. Doping of Pt/Al_2O_3 with CeO_2 increased the dispersity of platinum, suppressed deep oxidation and noticeably increased the activity and selectivity of the catalytic system in the POM. This reaction proceeded in accordance with the following redox mechanism:

$$CeO_2 + n\,CH_4 \longrightarrow CeO_{2-n} + n\,CO + 2n\,H_2,$$

$$CeO_{2-n} + \frac{n}{2}O_2 \longrightarrow CeO_2.$$

Partial oxidation of methane over an oxide catalyst ($CeO_2–ZrO_2$) was studied at 400–475 °C under steady-state conditions and in the transient regime.[49] The reaction products contained CO, CO_2, H_2, H_2O, CH_2O and HCO_2H and traces of C_2 hydrocarbons. The reaction proceeded *via* the intermediate formation of CH_2O.

Molybdenum and tungsten carbides constitute a novel class of POM catalysts. Molybdenum carbide, $\beta\text{-}Mo_2C$, is active only at elevated pressures; it is unstable at ordinary pressure. The oxidised species MoO_xC_y are formed on its surface. The degree of conversion of CH_4 at 900 °C and 0.8 MPa was 83%, and that of O_2 reached nearly 100%, which corresponds to the thermodynamic equilibrium.[50] The POM reaction occurs according to a redox mechanism with involvement of surface oxycarbides:

$$2\,MoOC + CH_4 \longrightarrow Mo_2C + 2\,CO + 2\,H_2,$$

$$Mo_2C + O_2 \longrightarrow 2\,MoOC.$$

Ni-Containing carbides also proved to be active and stable compounds.[51] The reaction of $Ni(NO_3)_2$ with WO_3 yields $NiWC_x$, which differs from both NiC and W in catalytic properties.

b. Mechanism

In the past years, the mechanism of catalytic POM was studied in considerably more detail than other methane reforming reactions. Numerous data suggest (see a monograph [8] and references cited therein) that this reaction occurs according to two mechanisms, *viz*., a stepwise mechanism where deep oxidation of methane to CO_2 and H_2O is followed by steam and carbon dioxide reforming, and a direct mechanism involving complete dissociation of methane and oxygen on the catalyst surface:

$$CH_4 \longrightarrow C_{ads} + 4\,H_{ads},$$

$$O_2 \longrightarrow O_{ads}.$$

This is followed by the interaction of the adsorbed atoms:

$$C_{ads} + O_{ads} \longrightarrow CO,$$

$$2\,H_{ads} \longrightarrow H_2.$$

The mechanism of POM was studied at the level of an elementary act in the analysis of the reaction of CH_4 with

adsorbed oxygen using the molecular beam method.[51,52] The Pt(110) facet occupied with O atoms with the structure (1×2) was irradiated with a beam of CH_4 molecules. CO_2 was formed at surface temperatures below 280 °C, while CO was formed at higher temperatures. This reaction also yielded H_2, but no H_2O was observed. Short-lived chemisorbed molecular oxygen was also detected.

With the use of a TAP (Temporal Analysis of Products) reactor for the study of POM over Pt/MgO, dissociation of methane over partly reduced Pt surface was revealed.[53] Adsorption of CO_2 included the formation of a weakly bound precursor that was further converted into a carbonate and a hydrogencarbonate. Under the reaction conditions, CO existed in two adsorption states, *i.e.*, weakly bound (mobile) and chemisorbed. Oxidation of CO occurred on oxygen islets. Under these conditions, surface oxygen is converted into subsurface oxygen and *vice versa*.

Two oxygen species were detected on the surface of Pt-catalyst using a TAP reactor.[54] If CH_4 and O_2 pulses were injected separately onto the catalyst at 600–1000 °C with considerable intervals between the pulses, the products formed were CO (94%) and H_2 (99%) at a degree of conversion of CH_4 of ~90%. Pulses of $CH_4 + O_2$ resulted in CO_2 and H_2O as the main products. It was thus concluded that the Pt surface contains stable subsurface oxygen and labile surface oxygen, the latter being involved in deep oxidation.

It has been shown[55] that the catalytic activities of the supported catalysts $Pt/Ce-ZrO_2$ are associated with their abilities to absorb and release oxygen. Removal of carbon from the catalyst is mediated by CeO_x and proceeds by a redox mechanism.

In the majority of cases, the kinetics of POM is of the first order with respect to methane and of the zero order with respect to oxygen. However, the zero order with respect to methane and an order larger than the first order with respect to O_2 were found over Pd/Si_4N_3 at 700–900 °C and at larger $CH_4:O_2$ ratios.[56] This suggests that CO is a primary product and the catalyst surface is predominantly occupied by carbonaceous compounds rather than by oxygen.

Partial oxidation of methane over Ni/Al_2O_3 was studied.[57–62] The IR spectra recorded after adsorption of methane at low temperatures revealed the presence of bands at 2998 and 3005 cm^{-1}, which were attributed to chemisorbed methane. These bands disappeared upon heating to 250 °C, and CO, H_2O, CO_2 and H_2 appeared in the gas phase, which suggests that these bands are due to intermediate species. Studies of temperature-programmed decomposition (TPD) of methane and IR spectroscopic studies showed that carbon was predominantly formed over Ni/Al_2O_3 as a result of the Boudouard reaction.[58] The decomposition rate of CH_4 passed through a maximum at ~700 °C.

The mechanism of POM over $Ni/\gamma\text{-}Al_2O_3$ was studied using the pulse method, TPD and XPES.[59] Under the reaction conditions (800 °C), the catalyst contained both Ni and NiO. The reduction of NiO began at 520–560 °C. The dissociation of CH_4 took place on the reduced centres and was followed by the reaction $C + O \rightarrow CO$ and the reduction of NiO by the carbon atoms. The use of the ion response method showed[60] that POM over Ni/La_2O_3 results in dissociation of methane and oxygen on Ni-centres to yield a carbide (Ni_xC) and an oxide (NiO), respectively. Their interaction yields CO.

Dissociation of methane occurs over a reduced catalyst $Ni/\gamma\text{-}Al_2O_3$ (direct mechanism), while oxidation of CH_4 to CO_2 and H_2O and the reduction of NiO to the metal over NiO/Al_2O_3 proceeded by a sequential mechanism.[61,62] The scheme below takes into account both mechanisms, but the direct mechanism is predominant.

$$Ni^0 + \frac{1}{2}O_2 \longrightarrow NiO,$$

$$CH_4 + 4\,NiO \longrightarrow CO_2 + 2\,H_2O + 4\,Ni^0,$$

$$CH_4 + Ni^0 \longrightarrow Ni\cdots C + 4\,H,$$

$$H + H \longrightarrow H_2\,(gas),$$

$$O_{ads} + Ni^0 \longrightarrow Ni^{\delta+}\cdots O^{\delta-},$$

$$Ni\cdots C + Ni^{\delta+}\cdots O^{\delta-}\ 2\,Ni^0 + CO,$$

$$2\,H + Ni^{\delta+}\cdots O^{\delta-} \longrightarrow Ni + H_2O,$$

$$CO + Ni^{\delta+}\cdots O^{\delta-} \longrightarrow Ni + CO_2,$$

The use of IR diffuse reflectance spectroscopy showed[58] that POM over Ni/La_2O_3 follows a sequential mechanism, but the direct mechanism is also possible at very low pressures of O_2. La_2O_3 forms oxycarbonates of the type $La_2O_2CO_3$, which favour removal of carbon from the surface of Ni. No decomposition of oxycarbonates occurs in a helium or oxygen atmosphere at 600 °C. This reaction also yields Ni, NiO and NiC phases. Presumably,[63] two routes of this reaction correspond to two limiting steps, *viz.*, dissociation of CH_4 and reaction of NiO with Ni_xC, which yields CO.

In the majority of studies devoted to the measurement of the kinetic isotope effect (KIE), *i.e.*, the k_{CH_4}/k_{CD_4} ratio, its value was more than unity. For the reaction $CH_4 + CO_2$ carried out over $Pt/\alpha\text{-}Al_2O_3$ at 550–650 °C resulting in CO, the k_{CH_4}/k_{CD_4} ratio was > 1; however, no KIE was observed in the direct POM.[64] It was concluded that it is the surface reaction between the adsorbed CH_x and O species, which yields CO, that is the limiting step, rather than the dissociation of CH_4. This implies that CO is formed by CDR ($CH_4 + CO_2$) or SRM ($CH_4 + H_2O$) rather than directly from CH_4 and O_2.

Studies of POM over Rh-foam, $Rh/\alpha\text{-}Al_2O_3$ or Rh/SiC using a TAP-reactor revealed[65–67] that the reaction occurs according to a sequential mechanism over fully oxidised Rh species, while on reduced species the reaction followed the direct route. With an increase in the O_2 pressure, the responses of CO, CO_2 and H_2O were shifted towards smaller residence times. The concentrations of the reaction products, *i.e.*, CO and H_2, increased as oxygen was removed from the catalyst surface.

The results of yet another IR spectroscopic study of the mechanism of POM in a TAP-reactor with Rh black as a catalyst suggest that at 700 °C the inhibition of dissociation of CH_4 was due to saturation of the metal centres with oxygen. Methane dissociated on reduced centres, whereas the newly generated carbon reacted with oxygen to yield CO_2. The role of active centres was played by partly reduced Rh^+ or dispersed Rh particles. The following mechanism was proposed:

$$CH_4 + (Rh) \longrightarrow CH_x(Rh) + \left(\frac{4-x}{2}\right)H_2$$
(methane activation),

$$CH_x(Rh) \longrightarrow C(Rh) + \frac{x}{2}H_2,$$

$$O_2 + (Rh) \longrightarrow 2\,O(Rh),$$

$$C(Rh) + O(Rh) \longrightarrow (Rh) + CO,$$

$$CH_x(Rh) + O(Rh) \longrightarrow$$

$$\longrightarrow CO_2 + \frac{x}{2}(H_2O/OH) + (Rh)\ \text{(deep oxidation)},$$

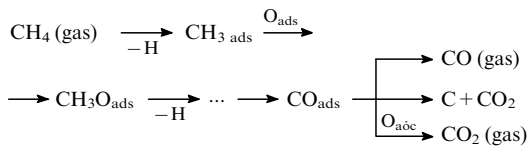
$$CH_x(Rh) + CO_2 \rightleftharpoons 2\,CO + \frac{x}{2}H_2 + (Rh)$$
(reverse Boudouard reaction),

$$CH_x(Rh) + H_2O/OH \rightleftharpoons CO + \left(\frac{x}{2}+1\right)H_2 + (Rh)\ \text{(reforming)},$$

$$(Rh) + O_2 \longrightarrow 2\,O(Rh)\ \text{(reoxidation)}.$$

The mechanism of POM over Pt/MgO was also studied using a TAP reactor.[68]

The POM reaction over Rh/SiO_2 was studied using TPD, IR and NMR spectroscopy and XPES.[69] Only the bands corresponding to CO adsorbed on the catalyst surface were observed in the IR spectra. Nevertheless, the following mechanism was proposed:



A more detailed study of the POM mechanism by IR and Raman spectroscopy *in situ*, made it possible to monitor CO, CO_2 and other oxygen-containing species on the surface. The Rh-catalysts were found to contain various forms of adsorbed CO, while adsorbed CO_2 and large amounts of O^{2-} were detected on the Ru catalysts. It was assumed that the direct reaction is the main route over Rh/SiO_2, while the consecutive mechanism (combustion → conversion) is more typical of reactions over Ru/SiO_2 and Ru/Al_2O_3.[70]

A surface compound with the adsorption band at 2000 cm^{-1} was observed in the IR spectra recorded *in situ* for POM over Rh/α-Al_2O_3 and Rh/δ-Al_2O_3.[71] Its concentration correlated with the rate of formation of CO. Presumably, the oxidation of CH_4 occurred *via* the surface hydride H−Rh−CO. Partly reduced oxide clusters with Rh^+ ions played the role of active sites. Hydrogen spillover occurs between Rh and the OH groups of the support. According to the KIE, over Rh/γ-Al_2O_3 at low (0.05%) concentrations of Rh, POM was mediated by a consecutive (combustion → reforming) mechanism.[72] At high concentrations of Rh (1%) and at temperatures below 500 °C, the mechanism of POM represented a combination of reforming and direct oxidation, while direct dissociation of methane was the dominant mechanism at temperatures above 650 °C.

A difference between the mechanisms of POM over rhodium and iridium catalysts was observed.[73–75] In the pulse injection ($2CH_4 + O_2$) onto Rh/TiO_2 and Rh/Al_2O_3, heating occurred of the upper layer of the catalyst, while in the case of Ir/TiO_2 this ocurred in the bottom layer. It was concluded that in the former case the reaction proceeded by a consecutive mechanism, which began with the most exothermic step of deep oxidation, whereas in the latter case the mechanism was direct. At 650 °C, Rh/TiO_2 exceeded all other catalysts in the catalytic activity.

The study of the reaction $CH_4 + {}^{18}O_2$ over Ru/SiO_2 and Ru/Al_2O_3 revealed [76] that in both cases POM proceeded by a consecutive mechanism. $C^{18}O^{16}O$ formed the first followed by $C^{18}O$ and $C^{16}O$.

According to the results of IR spectroscopic and isotope exchange ($^{16}O_2 - {}^{18}O_2$) studies carried out over Ca^{2+}-modified Ru/TiO_2 in a transient regime, the interaction of CH_4 with the Ru surface resulting in the formation of CH_x was a limiting step of POM.[77] The adjacent Ru sites and atomic oxygen are involved in the subsequent abstraction of H from CH_x. Initially, the CO molecule is formed in the interaction of carbon with oxygen on the Ru sites, while CO_2 is formed upon oxidation of CO on the oxidised sites. The IR spectra revealed the presence of bands corresponding to the OH groups (3600 cm^{-1}) and a broad band at 1995 cm^{-1} assigned to the carbonyl hydrides H−Ru−CO or H_2Ru−CO. The following reaction mechanism was proposed:

$$CH_4 \longrightarrow CH_x + H(S),$$

$$CH_x \longrightarrow C(S) + xH(S),$$

$$C(S) + O(S) \longrightarrow CO(S) \text{ or } CH_x + O(S) \longrightarrow CH_xO(S),$$

$$CH_xO(S) \longrightarrow CO(S) + xH(S),$$

$$CH_x + HO(S) \longrightarrow CH_{x+1}O(S),$$

$$CH_xO(S) \longrightarrow CO(S) + xH(S) \longrightarrow CO + \frac{x}{2}H_2 + (S).$$

Hereinafter, (S) is the surface. There are two different states for the Ru/TiO_2 catalyst under study, namely, the inactive state at low values of P_{CH_4}/P_{O_2} and the highly active and selective state (the selectivity is up to 90%) at higher values of the P_{CH_4}/P_{O_2} ratio. This selectivity increases with the increase in P_{CH_4}/P_{O_2} and temperature.

Theoretical calculations showed [78] that adsorbed oxygen favours the dissociation of CH_4 on Pt, Cu, Ag and Au, but not on Ru, Os, Ir, Rh or Pd. The differences in the selectivities of H_2 formation are associated with different stabilities of the OH groups on metals. Higher selectivity towards CO_2 is observed on oxygen-enriched surfaces. CO_2 is more readily formed over Ir, Pd and Pt than over Ru, Os and Rh. Low selectivity towards H_2 over Pd and Pt is attributed to the ease of the reaction:

$$2H(S) + O(S) \longrightarrow H_2O.$$

Kinetic simulation of gas-phase reactions over 0.3% Rh/α-Al_2O_3 under conditions of POM (780–1130 °C, 800 kPa) has been carried out.[79] Altogether, 40 elementary reactions were considered and the importance of the gas-phase reactions in the overall scheme was noted. Free radical uptake by the reactor walls or by an inert diluent (*e.g.*, non-porous Al_2O_3) inhibited reforming. In addition to synthesis gas, C_2 hydrocarbons were found in the gas phase The conversion of O_2 increased, whereas the selectivity towards C_2H_6 decreased upon dilution of the catalyst with an inert material.

Experiments carried out at the Institute of Chemical Physics of the RAS [80–82] have demonstrated that POM combines, in a complicated manner, both heterogeneous and homogeneous reactions. The so-called 'hot spot' formed on porous Ni-foam and Pt/ZrO_2 within a short (< 0.01 s) period of time after the loading of the reaction mixture at temperatures above 600 °C, which moved rapidly towards the gas flow into the frontal layer and even beyond it. If a quartz-glass wool pad is placed in front of the catalyst, its heating (~ 900 °C) exceeded that observed on the catalyst itself. Obviously, the catalyst generates reactive species (most probably, free radicals) which diffused towards the gas flow thereby triggering reactions in the gas-phase before the catalyst layer where the mixture was rich in O_2, but its content was insufficient to effect true gas-phase combustion. This reaction occurred in selectively and yielded predominantly $CO + H_2$, whereas CO_2 was formed in subsequent radical reactions:

$$CO + RO \longrightarrow CO_2 + R,$$

$$CO + RO_2 \longrightarrow CO_2 + R + O.$$

The overall selectivity of this process corresponds to the selectivity of the reaction occurring in the pre-catalyst layer and this can be modified, *e.g.*, by placing, in front of the active catalyst layer, a small amount of less reactive MgO where deep oxidation to CO_2 occurs. If the positions of the active catalyst and MgO are changed, no change in the selectivity is observed. No change in the selectivity occurs either if inert SiO_2 is placed in front of the catalyst.

Studies of the reaction $CH_4 + O_2$ over Pt/ZrO_2 in the presence of $^{13}CO_2$ revealed the absence of the label in the reaction products,[80–82] which suggests that the reaction follows a direct mechanism. However, the formation of ^{13}CO was observed over porous Ni, which occurs presumably [80] due to the redox reactions involving H_2, H_2O, CO, CO_2.

$$2Ni + O_2 \longrightarrow 2NiO,$$

$$NiO + CH_4 \longrightarrow Ni + CO + 2H_2,$$

$$NiO + CO \longrightarrow Ni + CO_2,$$

$$NiO + H_2 \longrightarrow Ni + H_2O.$$

Among those, only the first two reactions are related to POM. The key factor that determines the differences between the porous Ni and Pt/ZrO_2 is their different abilities to be oxidised by CO_2. This is probable for Ni, but is unlikely for Pt.

From the results considered in this Section one may state that the results of numerous studies into the mechanism of POM by physical methods, *viz.*, IR and Raman spectroscopy, XPES, the use of TAP-reactors, tracer technique and molecular beam methods, clearly indicate that this process occurs according to

two well-defined mechanisms, *viz*., direct and consecutive mechanisms. High temperature, short residence time and reduction of catalysts to the metals favour the former. At lower temperatures and prolonged residence times on the oxidised surfaces of supported catalysts, the oxidation of CH_4 occurs predominantly by a consecutive mechanism.

c. Technological features

The analysis of a kinetic model of POM over Pt/MgO revealed a high degree of heating at the reactor inlet due to deep oxidation of methane.[83] At the inlet temperature of 600 °C and the linear velocity of 3 m s^{-1}, the 'hot spot' was formed in the frontal layer with the temperature of up to 1400 °C at 0.1 MPa and up to 2200 °C at 2.5 MPa. The 'hot spot' temperature can be reduced using supports with high thermal conductivities (down to 1100 °C at 0.1 MPa and down to 1800 °C at 2.5 MPa).

An original reactor with a moving catalyst layer for conducting pilot-scale POM has been described.[84] Gas from a small nozzle enters the layer of a powdered catalyst ($Ni/La_2O_3/Al_2O_3$) to produce the spouted bed. The ejectile particles of the catalyst come in contact with the gas and fall down. The residence time is <0.5 s, the temperature is 850–1000 °C, the pressure is 0.2–0.8 MPa, the particle size varies from 120 to 150 μm.

The use of oxygen in POM is a crucial factor responsible for the high cost of synthesis gas and the explosive risk of the process. Therefore, considerable attention is currently given to technologies based on the use of heat-resistant O_2-permeable ceramic membranes. This makes it possible to combine the generation of synthesis gas and air separation and to avoid the use of expensive oxygen-generating equipment. According to the existing estimates, this technology saves from 20% to 50% of funds. The membranes must be strong, one of their surfaces must withstand temperatures above 900 °C in a highly oxidative atmosphere, whereas the other surface must be resistant to highly reducing media. In addition, the membranes must be resistant to poisoning, corrosion, deformation and differential pressure. Non-porous membranes were designed based on, *e.g*., perovskites ABO_3 with variable charges, where the size of one cation is comparable to that of the anion, while the size of the second cation is much smaller.[85] Replacement of one cation by another with a lower valence leads to the disbalance of charges and generates a vacancy $[\ ]_{O^{2-}}$. The ion flux through the membrane is proportional to $(\delta/L)\times(P_{O_2})_1/(P_{O_2})_2$, where δ is the membrane area, L is its thickness and $(P_{O_2})_1/(P_{O_2})_2$ is the concentration gradient of O_2 through the membrane. Membranes with improved characteristics exhibit a permeability (diffusion) plateau in the temperature range from 650 to 1000 °C. The appearance of hot spots and the generation of temperature gradients in such membranes is not hazardous. A high degree of conversion was achieved over a non-perovskite membrane ($SrFeCo_5O_x$) at 750–850 °C.

In 1997, five manufacturing companies (Amoco, BP, Sasol, Statoil and Praxair) launched an extensive research project devoted to the study of oxygen-permeable membranes for the preparation of hydrogen by the OTM Syngas (Oxygen Transport Membrane Synthesis Gas) process. The initial step of these studies is now complete.[86,87] Yet another research group (headed by Air Products Ltd.) including ChevronTexaco, Ceramatec and other partners, developed, in collaboration with the U.S Department for Energy, a technology for large-scale production of Ion Transport Membranes (ITM) for obtaining synthesis gas. These ceramic non-porous multicomponent membranes are prepared from metal oxides [perovskites $(La_xCe_{1-x})FeO_{3-y}$] with supported noble metals, they possess both ion and electron conductivities. The membranes operate at temperatures above 800 °C, at pressures up to ~30 atm and very high gas flow rates manifesting high selectivity towards oxygen. Considerable progress has been achieved in the choice of materials, design, manufacture of membranes and support of catalysts, which is prerequisite for the successful commercialisation of the ITM Syngas technology. The economic estimates testify to high potentials of this technology.[88]

Hydrogen-permeable membranes constitute yet another class of membranes for POM.[89,90] As for the O_2-permeable membranes, the addition of water vapour to CH_4 efficiently suppressed coke formation and increased the yield of the product. Hydrogen removal shifts the equilibrium and enables a high degree of conversion. Under specific conditions, pure hydrogen can be prepared containing no CO admixture. The use of membranes prepared from 5 μm-thick $Pd/Ag/Al_2O_3$ films also gave good results: at 578 °C, the degree of conversion exceeded the equilibrium value by 20%.

High production costs of synthesis gas and hydrogen stimulated the search for alternative methods of their preparation. Redox methods are based on separate interactions. Metals react with water vapour to give oxides and hydrogen, while the interactions of oxides with methane yield CO_2, H_2O and the metal. Such a reaction scheme is actually a modification of a classical iron steam procedure where hydrogen has been prepared by the reaction of iron with water vapour and iron oxide has been reduced by the producer gas. Nowadays, it is methane that is used as a reducing agent.

A cyclic POM process over the perovskite catalyst $La_{1-x}Sr_xFeO_3$ has been studied.[86] The catalyst circulated between two reactors at 800–900 °C. In one reactor, methane was oxidised into synthesis gas using the lattice oxygen, while in the second reactor perovskite was reoxidised by air. The duration of each cycle was several minutes. The main advantages of this cyclic process are explosion safety and exclusion of oxygen-generating units. Later, studies of a similar cyclic process over Ce, Zr, La and Sm oxides with supported Pt was carried out at the Institute of Catalysis of the Siberian Branch of the RAS.[55]

Some of the results on selective POM were reported at the 6th Natural Gas Conversion Symposium. Among various catalytic systems of the metal–oxide type explored by specialists of Snamprogetti, a pure iron–iron oxides system proved to be the system of choice.[91] The following reactions occur:

$$3\,Fe + 4\,H_2O \longrightarrow Fe_3O_4 + 4\,H_2,$$

$$3\,FeO + H_2O \longrightarrow Fe_3O_4 + H_2,$$

$$4\,Fe_2O_3 + CH_4 \longrightarrow 8\,FeO + CO_2 + 2\,H_2O,$$

$$Fe_3O_4 + CH_4 \longrightarrow 3\,FeO + CO + 2\,H_2.$$

The Snamprogetti technology enables the preparation of pure hydrogen without intermediate isolation of synthesis gas. Modified oxides $Cu-Cr-FeO_x$ and $Cu-Ni-FeO_x$ were also used for this purpose.[92] Additives to iron oxide decrease the temperature of FeO_x reduction from 600–700 to 300–400 °C and prevent sintering of the oxide. Copper and nickel also generate sites where the activation of methane takes place.

In studies of a similar system (PbO–Pb), the kinetics of PbO/Al_2O_3 reduction by methane in the temperature range 760–927 °C was investigated.[93] The reaction order with respect to methane was equal to 1; the apparent activation energy was ~40 kcal mol^{-1}. The degree of PbO reduction of 0.5–0.6 was the threshold as regards the selectivity of methane conversion: at lower degrees of reduction, CO_2 formed exclusively, while at higher degrees, the formation of CO was predominant.

3. Oxidation of methane at millisecond contact times

Oxidative catalytic reactions that occur at short (millisecond) contact times (τ) were known and have found industrial application (*e.g*., the Andrussov reaction: $NH_3 + CH_4 + O_2$) since the first half of the past century. Systematic studies of these reactions were carried out by Schmidt,[94,95] who has demonstrated advantages of hydrocarbon oxidation (including POM) over solid catalysts (gauzes, foamy metal blocks, open-channel blocks, *etc*.) at small contact times and, correspondingly, at high volume flow rates, which ensured very high productivity.

The catalytic oxidation of hydrocarbons over solid catalysts at low τ was especially efficient in simple small-size reactors; no carbon formation occurred.[94,95] High temperature and high concentration gradients are the characteristic features of such processes. As a rule, the temperature gradients are of the order of 10^6 deg s^{-1} and 10^5 deg cm^{-1}. These processes are autothermic and proceed under virtually adiabatic conditions, since the energy released in the exothermic reactions causes rapid heating of the gases and the catalyst to $\sim$1000 °C, whereas the heat release rate is far too high to enable effective cooling through the reactor walls.

The axial temperature profile in a millisecond reactor depends on the ratio of gas-phase and surface reactions. Very often, the reaction occurs in a two-zone mode; but the reactions on blocks and gauzes follow different mechanisms. In the first metal layers (1 μm thick) of block catalysts, highly exothermic oxidation of hydrocarbons into CO_2 and H_2O is accompanied by heating to temperatures above 1000 °C. If methane is used as a hydrocarbon, the reaction yields synthesis gas. Endothermic reactions, *e.g.*, direct dehydrogenation of C_2H_6 to C_2H_4, take place on the remaining solid. The addition of small amounts of hydrogen to an ethane–oxygen mixture resulted in 85% selectivity towards C_2H_4 over Pt–Sn-catalysts. At millisecond τ, only part of the molecules has sufficient time to come in contact with the surface of gauze-like or spiral catalysts, to be heated up to $\sim$900–1000 °C and oxidised. The rest of the molecules 'skip' the catalyst without being heated and interact with heated particles in the post-catalyst zone at intermediate temperatures. The formation of peroxy radicals and hydroperoxides is possible in this case.

At short contact times, the conditions for gas-phase reactions are difficult to predict because of high axial and radial concentration and temperature gradients. However, the switch from millisecond laboratory-scale reactors to industrial-type reactors is believed[94] to pose no problems. It is merely necessary to increase the diameter of the reactor with retention of the linear gas flow rate. It is suggested that the increase in the reactor diameter to 30 cm at a flow rate of 10^6 h^{-1} enables the daily output of several tons, while in reactors with a diameter of up to 180 cm the daily productivity can reach 1000 tons.

Non-linear processes, such as self-oscillations and autowaves in POM over nickel catalysts, were discovered by researchers of the Institute of Chemical Physics of the RAS.[80] The analysis of these phenomena prompts a conclusion that a crucial role in their appearance is played by oxygen and carbon accumulated in the catalyst.

A reactor based on a ceramic block with microchannels coated with Al_2O_3 and an Ni–Co–Cr–O alloy has been developed at the Institute of Catalysis of the Siberian Branch of the RAS.[96] The catalyst manifested high thermal and mechanical stability under conditions of high-temperature POM.

Stable and complete conversion of methane was achieved at 800 °C and a linear gas flow rate of 0.75–1.50 m s^{-1} in a reactor with a fluidised bed of a catalyst (Ni/α-Al_2O_3) designed for small contact times,[97] the yields of H_2 and CO constituted 97% of the thermodynamically permissible values. The design of a fluidised bed reactor has been described elsewhere.[98]

The mechanism of POM over a Pt gauze at 800–1100 °C was studied in a TAP reactor.[99] Experiments with alternating pulses of CH_4 and O_2 showed that CO and H_2 are the primary reaction products of CH_4 with O_2 over Pt. In the absence of gas phase O_2, the maximum attainable selectivities to CO and H_2 were 97% and 96%, respectively.

At low surface oxygen concentrations, oxygen incorporated in the Pt bulk diffuses to the surface and reacts with carbon to form CO, *i.e.*, a direct mechanism operates.

The oxidation of a microstructure honeycomb-like catalyst prepared from rhodium foil[100] in the presence of oxygen was carried out at 2 MPa. High thermal conductivity of Rh provided more efficient (in comparison with Pt–Rh gauzes) heat dissipation. The temperature of the catalyst under the reaction conditions reached 1080–1200 °C. The analysis of electron micrographs revealed signs of Rh corrosion upon POM.

The oxidative coupling and partial oxidation of methane were studied at $\tau < 5$ μs.[101] Over Rh/α-Al_2O_3, the selectivity towards C_2 products was rather low, but increased to 20% over Pt/α-Al_2O_3, acetylene being the major product. A peculiar temperature profile along the catalyst layer is believed to be the driving force of this process: the inlet temperature was 200 °C, and the outlet temperature was as high as $\sim$1500 °C.[102] Homogeneous reactions predominate at high temperatures. The scheme of methane oxidation into synthesis gas proposed in this study included 277 homogeneous and 19 heterogeneous steps. The conclusions based on the analysis of this model were compared with the experimental results obtained at 750–1150 °C and pressures of up to 3.5 MPa. It was established that homogeneous reactions were predominant at $\tau > 10$ ms, at high temperatures and at high pressures. The adiabatic heating reached 1365 °C, while the true 'hot spot' temperature in the catalyst layer measured by the emission thermography may be even higher.

It was shown[103] that the selectivity towards CO and H_2 was as high as 95% in POM and CDR over $Rh/MgO/Al_2O_3$ at 750 °C and at $\tau = 12$ ms. This catalyst appeared to be more selective than $Rh/MgO/Al_2O_3$, but the latter was more efficient in the activation of CH_4 and less efficient in the activation of O_2.

The temperature of the catalyst (> 650 °C) over Rh/α-Al_2O_3 at contact times < 12 ms was high enough to initiate POM or even carbon-dioxide reforming of methane. No synthesis gas was formed at $\tau > 12$ ms.

Studies into methane oxidation into synthesis gas over a Pt-gauze in the temperature range from 680 to 930 °C and at variable contact times (0.2–0.02 ms) revealed that the conversion of CH_4 and O_2 was limited by their transport to the catalyst, while the selectivity towards CO was determined by the reaction on the surface.[104] Hydrogen formation took place only at 1000 °C.

4. Carbon dioxide reforming of methane

a. Catalysts

Carbon dioxide reforming of methane (CDR) is carried out at higher temperatures ($\sim$900 °C) than SRM or POM. The interest in this reaction stems from the possibility of obtaining synthesis gas with the composition $CO : H_2 = 1 : 1$, which is required for the synthesis of dimethyl ether.

Similar to SRM and POM, supported nickel catalysts are used for CDR most often. In addition, catalysts based on Co, Fe, Pt, Pd, Rh and Ir have also found application for this purpose, as in SRM and POM processes. In numerous studies, the activities of metal catalysts on various supports were compared. Basic supports such as MgO, La_2O_3, *etc.*, better withstand poisoning than acidic ones and presumably are involved in the activation of CO_2. Bimetallic catalysts exceed monometallic catalysts in both the activity and stability. It was found[105,106] that the catalytic activities and stabilities of 2% Ni/La_2O_3 and 2% Ni/ZrO_2 increased substantially upon promotion with 0.2% Rh.

Japanese investigators[107,108] demonstrated very high activity of the catalyst $Ni_{0.03}Mg_{0.97}O$ and its resistance against carbon deposition. A comparison of catalytic properties of solid solutions of $Ni_xMg_{1-x}O$ and supported Ni/MgO catalysts revealed that significantly smaller amounts of carbon are produced over the former, which can be attributed to the small size of Ni particles, surface basicity and interaction of Ni with the support. The size of Ni particles in $Ni_{0.03}Mg_{0.97}O$ was 3–4 nm; that in $Ni_{0.10}Mg_{0.90}O$ and in Ni/MgO was 6–8 nm and 3–10 nm, respectively. The degree of reduction of the metal in 30% Ni/MgO was higher than in 10% Ni/MgO. According to X-ray phase analysis data, the catalyst comprised three phases, *viz.*, Ni, MgO and a solid solution with high content of NiO. The formation of carbon nanotubes was observed over Ni/MgO. The least changes during operation occurred in $Ni_{0.03}Mg_{0.97}O$.[109]

Researchers from the Institite of Chemical Physics of the RAS and the Institute of Petrochemical Processes of the Azerbaijan

Academy of Sciences established that CDR occurred over oxide Mn-containing catalysts.[110] Later, supported metal catalysts came to be used for this reaction. The reaction $CH_4 + CO_2$ was studied over various catalysts [Ni/α-Al_2O_3,[111] Co/α-Al_2O_3 (see Ref. 112) and Pt/α-Al_2O_3 (see Ref. 113)] in flow and pulse regimes using differential scanning calorimetry. Treatment of NiO/Al_2O_3 with hydrogen at 700 °C resulted in partial reduction of NiO to Ni. Methane virtually did not react with oxidised Ni or Co, but interacted actively with the reduced catalyst to give H_2 and surface carbon. With the lattice oxygen, the latter reacted slowly, but its reaction with adsorbed oxygen was fast. A fast rate was also characteristic of the reaction of CO_2 with surface carbon to yield CO, while the reaction with the metal (M) resulting in CO and MO was slow. It may thus be concluded that the main route of CDR over Ni/α-Al_2O_3 and Co/α-Al_2O_3 includes dissociative adsorption of CH_4 resulting in $C + 2H_2$ and the reverse Boudouard reaction of the carbon formed with CO_2. The side routes include the reactions of CH_4 chemisorption products with oxygen incorporated into a catalyst and dissociative adsorption of CO_2 on the metal. A competitive reaction of surface carbon with adsorbed oxygen reduced the degree of conversion of CO_2 in the main reaction; therefore, the rate of the reaction $CH_4 + CO_2$ decreased in the presence of O_2 due to oxygen poisoning of the catalyst.

A broad range of catalysts based on Ni/MgO has been studied.[114] High activity was observed for Ni/MgO doped with CeO_2, CuO, Cr_2O_3 and MnO_2. Under conditions of catalysis, these dopants underwent oxidation or reduction. Ni/MgO–Cr_2O_3 proved to be the most active catalyst. The degree of conversion over the catalyst 6% Ni–1% Cr_2O_3/MgO reached virtually the equilibrium value even at 700 °C. Even small amounts of Ni and Cr_2O_3 had a promoting effect on each other. The Co/α-Al_2O_3 system manifested high activity and stability in an analogous study [115] of supported cobalt catalysts.

The catalyst 5% Ni/CaO–Al_2O_3 prepared by deposition of nickel onto the preformed layer of aluminate $CaAl_2O_4$ manifested higher activity and was less subject to carbon deposition than the catalyst prepared by simple mixing of Ca, Ni and Al salts.[116] The differences observed were attributed to the formation of various amounts of NiO on the surface of these catalysts. The catalyst Ni/CaO–SiO_2 used in the study of CDR at 650 °C was prepared by impregnation of CaO-modified SiO_2 with Ni salts.[117] This procedure increased the metal dispersion. The carbon fibres formed caused deactivation of the catalyst.

The oxide ZrO_2 in the catalyst Ni/ZrO_2/MgO stabilised nickel on the support.[118] The reduction temperature of NiO increased with the increase in the MgO content. In the absence of MgO, the catalyst Ni/ZrO_2 was inactive, whereas the addition of only 1% MgO brought the conversion to virtually the equilibrium value.

Potassium promotes the activity of Ni/Al_2O_3. The addition of potassium had little effect on the dissociation rate of CO_2 and the reaction rate of CH_x with O_{ads}.[119] Potassium plays a role in dividing the Ni surface into small ensembles, thus carbon deposition is suppressed. The addition of MnO also inhibited carbon deposition.[120] The catalyst Ni–MnO_x/Al_2O_3 prepared by co-precipitation was more active than Ni–MnO_x/γ-Al_2O_3 prepared by impregnation and the above-described $Ni_{0.03}Mg_{0.97}O$.

The stable catalyst Ni/Al_2O_3 was prepared by repeated deposition of carbon from methane and subsequent elimination of carbon by treatment with carbon dioxide.[121] The assumption that active sites of the catalyst differ from those where carbon filaments are formed was the idea of this method. The repetition of the deposition–elimination cycles decreased the overall carbonisation.

The catalyst Ni/CeO_2–Al_2O_3 manifested higher activity than Ni/γ-Al_2O_3 and Ni/CeO_2.[122, 123] The addition of CeO_2 suppressed the interaction of Ni with the support, facilitated reduction and increased the dispersion of Ni. Owing to the addition of CeO_2, the carbon atom reacts more efficiently with oxygen-containing substances following dissociation of adsorbed CO_2 eventually resulting in a reduction of coke formation.

Perovskites $LaNi_xFe_{1-x}O_y$ effect complete conversion of CH_4 and CO_2 at 800 °C and are highly reactive catalysts for CDR.[124] Under conditions of the catalytic process, the mixed perovskite-type structures are destroyed, but at $x < 0.5$ these catalysts can be recovered by calcination. Ni–Fe alloys with variable compositions were formed at $0.3 < x < 0.8$. It was suggested that fusion prevented poisoning of the catalyst with carbon due to inhibition of carbon diffusion through Ni particles.

The catalytic activities and resistance of the perovskites $La_{1-x}Sr_xNiO_3$ ($x = 0.01$, 0.1) and $La_{2-x}Sr_xNiO_4$ ($x = 0.1$) against coke formation at 600 °C and ambient pressure depended on the type and stoichiometry of the perovskite.[125] Thus $LaNiO_3$ manifested high catalytic activity, while $LaNiO_4$ was totally inactive. $La_{0.9}Sr_{0.1}O_3$ and $La_{1.8}Ni_{0.2}NiO_4$ manifested the highest activity among strontium-substituted catalysts. Under CDR conditions, the catalyst was converted into a mixture of $La_2O_2CO_2$ and $SrCO_4$ with metallic Ni (X-ray phase analysis data). This may result from replacement of the lattice oxygen, which is accelerated in a reducing atmosphere at a ratio $CH_4 : CO_2 = 1 : 1$. Presumably, high activity was determined by the presence of two sites, *viz*., La_2O_3 responsible for the activation of CO_2, and Ni responsible for the activation of CH_4.

CDR over Ni catalysts supported on α-Al_2O_3, γ-Al_2O_3, $Al_2O_3 \cdot SiO_2$, SiO_2, MgO, ZrO_2 and modified with transition metals (Co, Cu, Fe) and alkaline promoters (Na, K) has been studied.[126] The catalytic activities of Ni/α-Al_2O_3 and Ni/γ-Al_2O_3 were very similar, but coke formation over the latter was faster by virtue of its acidic properties. According to the resistance against coke formation, the supports are arranged in the following order: α-Al_2O_3 > γ-Al_2O_3 > SiO_2 > $Al_2O_3 \cdot SiO_2$ > ZrO_2 > MgO. The activities of the catalysts doped with transition metals decreased in the following order: Ni–Co > Ni > Ni–Cu > Ni–Fe, while those of the catalysts containing alkaline promoters appeared as Ni > Ni–Na > Ni–K. Metal additives inhibit reduction of Ni, but enhance its dispersion. After 12 h operation in the absence of a modifier, the Ni-catalyst was completely deactivated, whereas the activity of the Ni–Co-catalyst increased noticeably with no coke formation. Cobalt catalysts were comparable to nickel catalysts in catalytic activity and stability,[126] Co/MgO/SiO_2 containing 50% MgO being the most active. The activity characteristics of Co/γ-Al_2O_3 were similar to those of Ni/γ-Al_2O_3. The stabilities and activities of Co catalysts depended on the concentration of Co and calcination temperature. At high cobalt content, deactivation occurred due to carbon deposition.

The activity of Co/TiO_2 strongly depended on the reduction temperature.[127] Only the catalyst reduced at $T > 850$ °C manifested high activity and stability. Doping with Pt and Ru improved these characteristics.

The activities and stabilities of catalysts prepared by support of Co, Ni, Ru, Rh, Ir and Pt on SiO_2 or Al_2O_3 at 400–750 °C have been studied.[128] The nature of the metal and, to a lesser degree, properties of the support were of critical importance. At 450 °C, deactivation was only observed over supported iridium, while at 750 °C other metals were deactivated due to sintering. Ni, Co and Rh were found to be the most resistant to deactivation. The activities of the catalysts supported on Al_2O_3 decreased in the following order: Rh > Ni > Ir > Ru > Pt > Co; the catalysts supported on SiO_2 manifested much lower activities.

Because of lesser solubility of carbon in the platinum-group metals, these were more active in CDR than Fe, Co and Ni and suffered less from carbon deposition [129] The CDR was performed over Ni-, Co-, Ru-, Rh-, Ir- and Pt-catalysts supported on SiO_2 and Al_2O_3 at low and moderate temperatures (400–800 °C). At 500 °C, only iridium catalysts were deactivated, while at 800 °C many catalysts underwent deactivation due to sintering. Ni-, Co- and Rh-catalysts manifested the highest stabilities. The activities of the tested catalysts decreased in the following order:

Rh > Ni > Ir > Ru > Pt. Catalysts supported on SiO_2 were much less active.

At 600 °C, Pt/ZrO_2, Rh/ZrO_2 and $Rh/\gamma\text{-}Al_2O_3$ manifested high activities and stabilities in CDR.[130] The activity of Pt/ZrO_2 was determined by the available perimeter of the supported platinum. In contrast, the activities of Rh/ZrO_2 and $Rh/\gamma\text{-}Al_2O_3$ depended on the concentration of surface Rh atoms rather than on the nature of the support. Pt/SiO_2 manifested a much lower activity. It was suggested that ZrO_2 favours the dissociation of CO_2 and, as a consequence, elimination of carbon.

As in POM, molybdenum and tungsten carbides were active in CDR at high pressures and at elevated temperatures.[131–133] According to activities at 950 °C and 0.8 MPa, the metal carbides are arranged in the following order: $Mo_2C \sim VC \sim WC > NbC > TaC$. The supported molybdenum carbides could be arranged in the following order of stabilities: $Mo_2C/Al_2O_3 > Mo_2C/SiO_2 > Mo_2C/TiO_2$. At low pressures, the oxidation of carbides resulted in their deactivation. Among other carbide catalysts (Mo_2C/SiO_2, WC/SiO_2, Mo_2C/Al_2O_2 and Mo_2C/ZrO_2), the former manifested the highest activity in CDR.[134] The conversion of Mo_2C into MoO_2 resulted in the deactivation of the catalyst. The activity of Mo_2C per mass unit of the catalyst was one or two orders of magnitude lower than the activities of metal catalysts due to its smaller specific surface.

However, despite extensive studies into catalytic systems, the overwhelming majority of papers are devoted to the analysis of only one type of active and stable CDR catalysts, *viz*., Group VIII metals (most often, Ni and Co supported on basic oxides, such as MgO, MnO and CaO). Rhodium catalysts possess the highest activities and stabilities, but they are very expensive. Of the oxide supports, preference should be given to moderately basic oxides that can undergo oxidation–reduction, *e.g.,* MnO. In the metal–metal oxide pair, the CH_4 is activated by the metal, while the oxide activates the CO_2 molecule.

b. Kinetics

The kinetic aspects of CDR on the material presented in more than 60 papers were discussed in 1996.[135]

The values of the activation energy, E_a, determined from the consumption of CH_4 and CO_2 vary from 30 to 350 and from 35 to 130 kJ mol^{-1}, respectively, while those determined from the yields of CO and H_2 are 30–318 and 38–250 kJ mol^{-1}, respectively. The largest out-of-order value of E_{CH_4} was noted for reactions carried out over Re/Al_2O_3 (350 kJ mol^{-1}). It is suggested [135] that the values of E_a obtained for the reaction carried out over Pt/MgO [136] should be excluded from the reliable data. In this study, $E_{CO} > E_{CH_4}$, whereas in all other papers this ratio was the opposite. Also, E_{CO} was found to be equal to 921 kJ mol^{-1}, although this value usually amounts to 230 ± 20 kJ mol^{-1}, *i.e.,* similar to the values of the energy of activation of cracking of CH_4 over Ni(110) and Ni(111) (233 ± 27 and 221 ± 20 kJ mol^{-1}, respectively). The E_a values for the catalytic reactions over noble metals are usually close to 314–337 kJ mol^{-1}. The apparent energy of activation strongly depends on the degree of the steam conversion of CO, which seems to be manifested in larger E_{CO} upon an increase in the space velocity. The degree of conversion decreases considerably, and the effect of the reverse reaction, *i.e*., hydrogenation of CO to CH_4, becomes less significant.

The data on the activities of different catalysts expressed as the reaction turnover number (t.n.) at 450 °C are documented.[135] The t.n. values obtained by extrapolation vary from 0.1 to 1, but are higher for Ru/TiO_2 (4.3–7.3) and Ru/Al_2O_3 (1.5–4.3) catalysts. The t.n. values for reactions over Rh crystals on different supports decrease in the following order:[137] $ZrO_2 > TiO_2 > Al_2O_3 > La_2O_3 \sim SiO_2 > MgO$.

In the overwhelming majority of studies, the rate of CDR was directly proportional to P_{CH_4}, whereas P_{CO_2} enters the kinetic equations cited in certain papers as both a numerator and a denominator with the exponent n varying from 0 to 2.[138]

The positive kinetic isotope effect k_{CH_4}/k_{CD_4} observed in CDR over $Ni/\gamma\text{-}Al_2O_3$,[139] Ni/SiO_2 (see Ref. 140) and Ni/La_2O_3 catalysts [141] suggests that the reaction of oxygen with the catalyst is the limiting step, whereas dissociation of CO_2 is a rather smooth process. The KIE value over Ni/Al_2O_3 and Ni/La_2O_3 increases with temperature, being much larger over Ni/La_2O_3 than over Ni/Al_2O_3.

A highly dispersed, firm and stable catalyst $Ni/La/\alpha\text{-}Al_2O_3$ is particularly suitable for performing CDR in a fluidised bed.[142] At 700–900 °C and 16–40 kPa, the activation energy of this reaction was 90 kJ mol^{-1}. According to the kinetic Langmuir–Hinshelwood model proposed for this reaction, the equilibrium is achieved at longer contact times. CDR in a fluidised bed reaction was carried out over $Ni_{0.15}Mg_{0.85}O$ (see Ref. 143). Inhibition of carbon deposition even at elevated pressures can be attributed to carbon gasification. The electron micrographs of the catalyst show the presence of carbon filaments formed by the catalyst in the fixed bed reactor. No such effect is observed in the fluidised bed reactor.

c. Mechanism

Numerous studies have shown that carbon formation and its reactions on the metal surfaces are the crucial factors in the mechanism of CDR. The most popular concept consists of the formation of adsorbed C, H, O, CO species on the surface and their reactions with each other that yield CO and H_2.[135] Carbon oxide is formed from methane or CO_2.

$$CO_2 + (S) \rightleftharpoons CO + O(S),$$

$$CH_4 + (S) \longrightarrow CH_x(S) + (4-x)H(S) \longrightarrow C(S) + 2H_2,$$

$$C(S) + O(S) \longrightarrow CO(S) + (S),$$

$$CO(S) \rightleftharpoons CO + (S).$$

A kinetic model for the formation and gasification of carbon over nickel catalysts under conditions of CDR and SRM has been discussed.[144, 145] At 500–550 °C, carbon filaments were formed predominantly by the Boudouard reaction. This reaction was accelerated in the presence of alkali concomitantly with an increase in the surface concentration of oxygen and a decrease in the lumped forward rate coefficient for the methane cracking. The gasification of filamentous carbon was effected by CO_2, H_2O and H_2. Two competing processes, *viz*., growth of carbon filaments (nanotubes) involving carbon dissolution in Ni, diffusion and segregation of carbon on the opposite side of the particle and shortening of the filaments due to gasification.

The data from XPS, Auger spectroscopy and CDR by the pulse method suggest transient formation of carbides over cobalt catalysts.[146] Similar results were obtained in experiments over Ni/La_2O_3, $Ni/\gamma\text{-}Al_2O_3$, Ni/CaO and $Ni/CaO-La_2O_3$ using $^{13}CH_4$ and $C^{18}O_2$ as the reactant gases.[147, 148] The formation of nanotubes from carbon is also possible. Presumably, the active sites of the catalyst Ni/La_2O_3 lie at the boundary between Ni and La_2O_3, where the following reactions occur:

$$CH_4 + Ni \longrightarrow NiC + 2H_2,$$

$$CO_2 + La_2O_3 \longrightarrow La_2O_2CO_3,$$

$$La_2O_2CO_3 + Ni \longrightarrow La_2O_3 + CO + NiO,$$

$$NiC + NiO \longrightarrow 2Ni + CO.$$

These data suggest that cracking of CH_4 over Ni/La_2O_3 occurs over Ni and is a limiting step, whereas the activation of CO_2 occurs on La_2O_3. In contrast, the activation of CO_2 over Ni/Al_2O_3 is a slower step than that of CH_4.

The mechanism of the initial steps of CDR over $NiSiO_2$, La_2O_3 or $La_2O_3 \cdot SiO_2$ was studied by the pulse response method.[139] The adsorption of CO_2 on NiO competed with the cracking of CH_4. The adsorption of carbon dioxide on La_2O_3 resulted in the formation of formates and carbonates, which

further decomposed with evolution of CO and recovery of the oxygen vacancies. The oxygen required for the formation of CO from CH_4 is provided by its transfer from La_2O_3 to Ni. Methane reduced NiO and formed vacancies in La_2O_3.

The CDR reaction over $Ni-La_2O_3$/zeolite (5 Å) was studied by X-ray diffraction spectroscopy, Fourier-transform infrared spectroscopy *in situ*, transmission electron microscopy (TEM), EPR and using chemical traps.[149,150] Carbon formation from CH_4 and CO upon its disproportionation was confirmed in experiments with $^{13}CH_4$, and the contribution of CO increased at higher temperatures. According to TEM data, the bulk of carbon was deposited in the form of carbon nanotubes. Enhanced adsorption of CO_2 was observed in the presence of hydrogen. In experiments with pulsed injection of methane following reduction of the catalyst with hydrogen it was shown that the surface oxygen favoured cracking of CH_4. The use of chemical traps (CD_3I) and infrared diffuse reflectance spectroscopy established the formation of CD_3CO_2H and CD_3CHO. In experiments with CH_3I as a trap, HCO_2 or CH_xO were detected as intermediates in the formation of CH_3CO_2H. The dissociation of the C–H bond in CH_xO is a slow step, which suggests the formation of reactive intermediates HCO_2 and HCO. The number of converted CO_2 molecules was nearly proportional to the number of hydrogen atoms on the catalyst, which suggests that the activation of CO_2 occurs with the involvement of H_{ads}. The larger degree of conversion of CH_4 on a CO_2-treated catalyst suggests the involvement of oxygen in the cracking of CH_4. IR spectroscopic studies *in situ* of the CDR mechanism over Rh/Al_2O_3 revealed [54] that the linear form of the adsorbed CO_2 is the active form that generates the reaction product.

Over Rh/α-Al_2O_3, the dissotiation of CH_4 proceeds in the same manner as over Ni or Co, but the mechanism of CO_2 activation is different.[151] Unlike carbide or filamentous carbon formed over Ni or Co, the carbon formed over Rh is of a 'graphite' type and possesses low activity. CO_2 is neither activated on such a carbon, nor reacts with it. Presumably, a short-lived carbon, which differs from the graphite-type carbon, is formed initially and reacts with CO_2. It is this carbon that may represent a true intermediate of CDR. Oxygen acts as a poison over Ni or Co catalysts, whereas over Pt catalysts it activates CDR by eliminating the graphite-type carbon.

The CDR reaction over Pt/ZrO_2 and ZrO_2 was studied in a TAP-reactor using IR spectroscopy.[152,153] At 700 °C, the adsorption of CH_4 and CO_2 occurred independently of one another. The CH_4 cracking products over Pt/ZrO_2 and ZrO_2 abstract oxygen from ZrO_2. In an excess of oxygen, CO_2 was formed. The selectivity towards CO or CO_2 is determined by the same reaction:

$$CO_{ads} + O^* \rightleftharpoons CO_{2\,ads}$$

and depends on the surface contentration of oxygen. Under the reaction conditions, adsorption bands corresponding to carbonates CO_3^{2-}, bidentate carbonates, linear CO and OH groups were observed in the IR spectra. After administration of CO_2 pulses, only surface OH groups remained on the catalyst, but those were nonreactive. Obviously, the O^*_{ads} which remained after adsorption of CO_2, reacted with CH_4. The nature of the O* species has not been established; O_{ads}, OH_{ads} and even $CO_{3\,ads}$ groups may have to do with these. Over Pt/ZrO_2, methane dissociated into C_{ads} and H_{ads}, but no such dissociation was observed over ZrO_2. Probably, ZrO_2 is partly reduced to form an alloy $Pt_{1-x}Zr_x$, where the activation of CO_2 occurs. The following reactions take place on Pt/ZrO_2:[152]

$$CH_4\,(gas) \longrightarrow CH_x(Pt), \quad (1)$$

$$CH_x(Pt) \longrightarrow C(Pt) + x\,H(Pt), \quad (2)$$

$$C(Pt) + O(ZrO_2) \longrightarrow CO(ZrO_2) + O(ZrO_2), \quad (3)$$

$$CO_2(gas) + [\,]_O \longrightarrow CO(ZrO_2) + O(ZrO_2), \quad (4)$$

$$2\,CO_2(gas) \longrightarrow CO_3^{2-}(ZrO_2) + CO(ZrO_2), \quad (5)$$

$$CO_3^{2-}(ZrO_2) \rightleftharpoons CO(ZrO_2) + 2\,O(ZrO_2), \quad (6)$$

$$CO(ZrO_2) \rightleftharpoons CO(gas), \quad (7)$$

where $[\,]_O$ is the oxygen vacancy in ZrO_2. The adsorbed hydrogen atoms form OH groups with surface oxygen, which serve as the sources of H_2 and H_2O. Substitution of CO_2, which yields CO [reaction (4) in the scheme above], for the lattice oxygen vacancy, is the limiting step of this process.

A large series of investigations of CDR over Ni/SiO_2, Ni/La_2O_3, Ni/Al_2O_3, Ru/SiO_2 and Ru/Al_2O_3 were carried out using isotope exchange, XPS, IR spectroscopy, ferromagnetic resonance and electron microscopy.[128,152–164] It was found that cracking of CH_4 over Ni/SiO_2 resulted in the formation of H_2 and accumulation of carbon on the surface. Cracking of $^{13}CO_2$ results in the instantaneous formation of gaseous ^{13}CO and adsorbed oxygen. The latter reacts with ^{12}C derived from $^{12}CH_4$ to produce a second molecule of carbon monoxide (^{12}CO) (the limiting step). Cracking of CH_4 was the slowest step over Ru, while CO_2 reacted directly with carbon to give two CO molecules. Administration of $^{13}CO_2$ and $^{12}CH_4$ pulses produces two output pulses, *viz.*, ^{12}CO and ^{13}CO. Alternating pulses of CO_2 enabled the removal of all the adsorbed carbon as a result of which the reaction rate dropped down to zero. In this case, the amount of oxygen accumulated on the surface was the lowest, which inevitably led to the inhibition of oxidation of H_2. Silicon dioxide is a rather inert support and does not take part in CDR.

Using the TAP-reactor method, it was proved that the support carbon of the Ru/C catalyst reacted with CO_2. In Ru/C doped with MgO, $MgCO_3$ was formed in the vicinity of Ru, which favoured the oxidation of carbon following cracking of methane. The OH groups at the MgO–Ru boundary prevented deactivation of the catalyst.

The following redox mechanism of CDR over Ni-catalysts has been proposed.[114] The oxidation and reduction of the NiO constituent of the catalyst ($NiO-Cr_2O_3-MgO$) occurs *via* a spinel according to the overall stoichiometric equation:

$$NiO + Cr_2O_3 \longrightarrow NiCr_2O_4,$$

$$NiCr_2O_4 + H_2 \longrightarrow Cr_2O_3 + Ni + H_2O.$$

Apparently, cracking of methane and activation of CO_2 occur over Ni or NiC.

$$CH_4 + Ni \longrightarrow NiC + 2\,H_2,$$

$$CO_2 + Ni \longrightarrow NiO + CO.$$

Over different catalysts, the mechanisms of CDR differ: over pure metals or over metals on neutral supports of the SiO_2 type, complete cracking of CH_4 and CO_2 is more probable, whereas on metals on basic supports the reaction proceeds *via* intermediate carbonates.

The intermediate formation of methyl radicals in CDR has been proposed. The free radicals CH_3 generated upon decomposition of azomethane were adsorbed on the catalyst (Rh/SiO_2) in order to elucidate this possibility.[165] Using IR spectroscopy, it was established that CH_3O_{ads} species formed reacted with CO_2 in the gas phase at temperatures above 10 °C. No coke deposition on the catalyst occurred. Under these conditions, the major part of CH_3 was adsorbed on SiO_2, while Rh took part in further conversions. The presence of CH_3 radicals on the surface of Ni/SiO_2 under conditions of CDR was confirmed by TPR and TPD.[166] In addition, C_2H_6 was also formed. Surface CH_3 radicals reacted with adsorbed oxygen atoms to give CH_xO and further CO and H_2.

The majority of experimental results suggest the double-centred mechanism of CDR where CH_4 is activated on the metal components of the catalyst with cracking into $C + 2\,H_2$ (or $CH_x + H_2$), while the activation of CO_2 is mediated by the oxide component. The reaction product (CO) is formed in two ways, *viz.*, by oxidation of the surface carbon and by reduction of CO_2.

On the surface, carbon is formed by two reactions, *viz*., cracking of CH_4 and the Boudouard reaction. On transition metal oxides supported on basic oxides, CDR can follow a redox mechanism.

d. Technological features

Attempts have been undertaken to separate the steps of CH_4 and CO_2 activation by carrying out CDR in a membrane reactor.[167] A Pd/Al_2O_3 membrane was prepared by electrodeposition of the metal on the support. At 350–600 °C, the degree of CH_4 conversion was 4%–20% larger than in a conventional process with the same catalyst, and the yield of H_2 increased from 3% to 18%. However, the operation of the membrane is strongly affected by coking and the expediency of its application was not presented.

CDR and POM were carried out using the oxygen-permeable membrane $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O$.[168] The degree of conversion of CH_4 and the selectivity towards CO exceeded 98% under oxygen conversion at 850 °C and at high $CH_4:O_2$ ratios. High activities and selectivities of CDR carried out at 900 °C were achieved. The use of a $CH_4 + CO_2 + O_2$ mixture for over 100 h ensured stable conversion of CH_4 (90%–92%) and CO_2 (94%–96%) with the selectivity towards CO close to 100%.

The feasibility of membrane isolation of pure hydrogen from synthesis gas in the CDR process over Ni/La_2O_3, $Ni–Rh/La_2O_3$,[105] Ni/ZrO_2 and $Ni–Rh/La_2O_3$ [106] is under study. At 700 °C, bimetallic Ni–Rh catalysts were much more active than monometallic catalysts, but monometallic Rh was found to be more stable.

5. Autothermal reforming (ATR)

The combination of two or three routes of oxidative reforming of methane, *viz*., SRM, POM and CDR, can result in the increase in the efficiency of raw material utilisation, in improvement of the thermal balance and control over the composition of synthesis gas. To this goal, one-pot exothermic deep oxidation of CH_4 and endothermic SRM and/or CDR are often performed. The technological process in ATR reactors includes two consecutive steps, *viz*., deep oxidation of methane followed by CDR + SRM with subsequent conversion of water gas.

The autothermal reforming of methane at high pressures (4–10 MPa), which meets the demands for subsequent synthesis of methanol and dimethyl ether, is discussed.[169] Its first step consists of combustion of CH_4 in a gas burner, and the second step includes CDR and SRM in a fluidised bed of a catalyst. Calculations show that the outlet temperature should be increased with an increase in pressure, but this may result in sintering of the catalyst and destruction of the fluidised bed. The kinetic calculations made account of 49 intermediates and 277 elementary reactions including those involving C_2 hydrocarbons. Lower yields of C_2H_2 and reduced soot formation are the beneficial effects of the elevated pressures.

The oxygen–carbon-dioxide reforming of methane over Pt/ZrO_2, Pt/Al_2O_3 and Ni/Al_2O_3 were studied in the temperature range of 550–800 °C.[170] At all temperatures, the yields of CO and H_2 from $CH_4 + CO_2 + O_2$ mixtures (the content of O_2 varied from 3% to 11%) were higher than in the case of the $CH_4 + CO_2$ mixture, and carbon deposition was smaller. Besides, these conditions facilitated control over formation of the hot spot on the catalyst. From a mixture containing 11% of O_2, the yields of CO and H_2 were nearly the same as those achieved upon oxidative reforming, $CH_4 + O_2$ (95% at 800 °C).

The combination of POM, SRM, CDR and deep oxidation of methane in one reactor is the most promising approach to autothermal reforming of methane. The main problem in the design of such reactors is connected with the differences in temperatures of these reactions, which brings forth the necessity for the spatial separation of heat-evolving and heat-adsorbing sites of the catalyst. One of the possible clues to the solution of this problem came from a group of Japanese investigators who performed the conversion of a $CH_4 + CO_2 + O_2$ mixture in a fluidised bed. However, it was not always possible to obtain the target $CO + H_2$ mixture with the required composition.

It was found[171] that the addition of CO_2 to the $CH_4 + H_2O$ mixture optimised methanol synthesis. Thus, the use of carbon dioxide reforming of methane instead of steam reforming reduces the cost of the technological process. However, this process is commercially profitable if only large amounts of relatively pure CO_2 are available. The $H_2:CO = 2:1$ ratio required for methanol synthesis is achieved at $CO_2:CH_4 = 1:3$ in accordance to the stoichiometry of the reaction:

$$3\,CH_4 + CO_2 + 2\,H_2O \longrightarrow 8\,H_2 + 4\,CO.$$

In 2002, a pilot plant for synthetic liquid hydrocarbons (SLH) with the daily capacity of 7 barrels was put into operation in Japan for trials of a novel catalyst for combined CO_2/H_2O reforming and assessment of a JNOC (Japan National Oil Corporation) technology based on this catalyst. The process is carried out in a tubular converter that requires no addition of oxygen. Synthesis gas thus produced is well-balanced with regard to the H_2/CO ratio for manufacture of SLH, methanol and dimethyl ether. The energy consumption is lower than in conventional processes at smaller CO_2 and H_2O molar ratios with respect to carbon in the supplied gas. It is expected that this technology will be especially efficient for the application to small fields with high content of CO_2 in the natural gas as well as for reprocessing of effluent gases rich in CO_2 and at liquefied gas plants.[172]

A heat-integrated ATR reactor with a Rh/Al_2O_3 catalyst is described.[173] The catalyst was applied onto the inner and outer surfaces of a ceramic tube. A $CH_4 + O_2$ flow was first fed inside the tube where deep oxidation of methane occurred and then onto the outer surface of the tube where CDR and SRM took place. This method allows a significant reduction of the 'hot spot' temperature in the reactor (below 900 °C). This process can be optimised by varying the number of catalyst layers on the inner and outer surfaces of the tube.

The mechanism of autothermal reforming over Pt/CeO_2, Pt/ZrO_2 and $Pt/CeZrO_2$ catalysts has been considered.[174] This reaction proceeds by a consecutive mechanism, *i.e*., the combustion of methane is followed by steam and carbon dioxide reforming of the unburned gas. $Pt/Ce_{0.18}Zr_{0.82}O_2$ is the catalyst of choice, it possesses high oxygen capacity, which is beneficial for the redox process. In the absence of CeO_2, the catalyst undergoes rapid deactivation.

The interest in the production of synthesis gas and hydrogen from higher hydrocarbons (including liquid hydrocarbons) is steadily increasing in connection with the prospects of broad use of hydrogen in motor transport. Steam and autothermal reforming of n-heptane were carried out over 15% Ni/Al_2O_3 at 700 °C.[175] At lower temperatures, thermal cracking occurred. An active and selective catalyst for steam reforming of ethanol into synthesis gas was obtained by doping a Cu–Zr-fluorite catalyst with cobalt.[176] Reduction of Co led to the generation of Co nanoparticles able to react with oxides. It was also shown that high (26%–27%) selectivity towards H_2 can be achieved in gas-phase oxidation of methane catalysed by NO_x (20% CH_4, 10% O_2, 0.06% NO).[177] The degree of methane conversion in a flow-through quartz reactor at 700–800 °C and the residence time of 0.6–3.7 s was 34%.

III. Partial oxidation of methane to oxygenates

1. Homogeneous oxidation of methane and ethane

Studies into kinetics and mechanism of homogeneous partial oxidation of methane to methanol (Direct Methane to Methanol, DMTM) and kinetics of partial oxidation of the nearest methane homologues are underway. The key features of the mechanism, optimum reaction conditions and actual yields of oxygenates upon methane oxidation in laboratory flow reactors were established [178–180] and the effects of pressure on partial oxidation of methane to methanol were analysed.[179] The most important

factors include a critical transition to a steady-state chain-branched mode,[8] increasing role of nonlinear gas-phase reactions and change in the relative contribution of heterogeneous processes.

The chain-branched oxidation process has a pronounced nonlinear character, the increase in the overall pressure accompanied by the increase in partial pressures of the reactants not only accelerates the reaction, but also increases the contribution of nonlinear gas-phase methanol-yielding processes. A decrease in the diffusion rate with an increase in pressure decreases the contribution of heterogeneous processes leading to the predominant formation of deep oxidation products. Studies on direct homogeneous oxidation of methane in laboratory-scale stainless steel and quartz flow reactors at 15–80 atm demonstrated the considerable effect of the reactor surface material on the oxidation process.[179]

A complex study of the dependence of the main parameters of the DMTM process on such factors as pressure, temperature, CH_4/O_2 ratio and the extent of dilution with the inert gas has been carried out.[181] The experiments were performed in fused-quartz reactors (1–10 mm in diameter) at residence time of ~10 s and complete conversion of oxygen. The experimental results are in good agreement with the known data.[8,181] At pressures around 100 atm and the $CH_4 : O_2$ ratio of 16.3 in a gas mixture containing 63% of He, the yields of the major reaction products (CH_3OH, CO, CO_2 and H_2O) exceeded 95%. No identification of other reaction products was carried out in this study. At temperatures above 460 °C, the degree of oxygen conversion increased jumpwise to 100%. The degree of methane conversion virtually paralleled the oxygen content in the mixture. The mean selectivity towards methanol was ~50%, which corresponded to the published data. It is of note that the optimum (in the authors' opinion) selectivity was reached at relatively high (~6% with respect to methane) oxygen concentrations. The selectivity towards CO was, on average, 3 times as great as that in CO_2. At temperatures above threshold values, the selectivity towards methanol passed through a small maximum at ~470 °C with subsequent monotonic decrease with an increase in temperature (35% at 490 °C).

As in the majority of previous studies, the drop in pressure was accompanied by a rapid decrease in the selectivity towards methanol (35% at 17 atm) and an increase in temperature (535°C at 17 atm) at which the maximum selectivity was reached. Further dilution of the reaction mixture with He resulted in an increase in temperature required for complete conversion of oxygen from 445 °C in the absence of helium to 530 °C in the presence of 80% helium. At a He content of 90%, no reaction occurred even at 554 °C. It is noteworthy that the monotonic increase in the selectivity towards methanol occurred with a decrease in the degree of dilution (from 35% at 80% of He to 63% in the absence of He). The reason should be sought in the drop of the reaction temperature rather than in the dilution itself. As in the previous studies,[178–180] the selectivity towards methanol increased with an increase in the $CH_4 : O_2$ ratio.

The tenfold increase in the reactor diameter required an increase in the reaction temperature to 495 °C, which is apparently due to higher activation energy of the homogeneous generation of radicals in comparison with the generation in a heterogeneous reaction. This was accompanied by a slight increase in the selectivity towards methanol, which is quite natural, taking into consideration the role of the catalytic formation of methane deep oxidation products on the catalyst surface. Under these conditions ($\leqslant$ 500 °C, residence time ~10 s), relatively high ($\leqslant$ 25% for CO and $\leqslant$ 8% for CO_2 with respect to methane) concentrations of carbon oxides had virtually no effect on either the degree of methane conversion or the selectivity towards methanol. This followed from virtually complete coincidence of experimental results obtained after a single passage of the mixture through the reactor and with recirculation of gases after separation of methanol and water.

Among recent studies of the DMTM process, special mention should be made of experiments carried out by Zhang *et al.*[182] Gas-phase oxidation was carried out in a flow reactor with a quartz insertion having an internal diameter of 6.7 mm and a heated area diameter of 270 mm at variable pressures (1.0–5.0 MPa) and temperatures (380–500 °C). Special attention has been given to exclusion of interactions of the reactants and reaction products with the metallic surfaces of the reactor and the thermocouple. The composition of the reaction products (CH_3OH, CO, CO, C_2H_6 and C_2H_4) was quite typical of this reaction except for the absence of formaldehyde.

A sharp increase in the degree of conversion of the reactants with an increase in temperature and the relatively weak effect of temperature on the yield of methanol after complete conversion of O_2 is consistent with the results of previous studies[8,180,181] and is characteristic of temperature dependences of the yield of CH_3OH in the branched-chain partial oxidation of methane. A decrease in the yields and selectivity towards methanol at temperatures above 480 °C at low jet velocities and the residence times in the heated zone of 45–90 s in reactors with small diameters can be attributed to the heterogeneous decomposition of CH_3OH. In any case, noticeable decomposition of methanol over Pyrex was observed under similar conditions even in the temperature range of 475–500 °C (see Ref. 8). The absence, from the reaction products, of formaldehyde, which is normally formed under conditions mentioned but is less resistant to heterogeneous decomposition, seems to be due to the same reason.

The results obtained suggest[182] that the degree of conversion of oxygen becomes smaller than 100% with an increase in temperature. The presence of small amounts of oxygen in the final products was observed in previous studies[8] and seems to be due to heterogeneous decomposition of oxygen-containing products, *e.g.*, peroxides.

The relatively high yield of methanol reported[182] correlates to some extent to the results reported by other authors.[183,184] It is noteworthy that in these studies the residence time was $\leqslant$ 1 min at relatively low temperatures, pressures and sizes of reactors with quartz or sapphire surfaces insulating the metallic parts of the reactor. These results are at variance with both those obtained at higher flow rates of the reactants and the results of kinetic simulation of a gas-phase process,[8] which suggests that in this case heterogeneous processes occurring on the reactor surface play a more prominent role. At temperatures and pressures mentioned above, neither quartz nor Al_2O_3 can be regarded as inert materials with respect to the reacting methane–oxygen mixture, although the mechanisms and rates of surface processes differ substantially from those occurring on the metal surface. The relatively low temperatures used in these studies also favour an increase in the contribution of heterogeneous reactions into the overall homogeneous–heterogeneous process of methane oxidation.[8] The residence time may be regarded as high, if one takes into account the rates of radial and axial diffusion, and this may rationalise the pronounced effect exerted by the presence of even insignificant metallic parts in any zone of the reactor. If this is true, the experimental results, which seem encouraging at the first glance, give unfortunately no grounds for the favourable assessment of the prospects of implementation of the process on an industrial scale, since it envisages, in principle, the use of very slow flows and high surface-to-volume ratios.

To date, the mechanism of the gas-phase DMTM process is generally understood. Numerous experiments showed that the selectivity towards methanol can reliably reach the level of 50% in flow-type reactors at ~450–500 °C and pressures $\geqslant$ 70–80 atm with a residence time of several seconds where the degree of methane conversion per cycle is 5%–6%.[8,180] Practical implementation of this process requires apparently that the main efforts are directed at improving the process technology to make use of its obvious benefits (simplicity, stability, non-susceptibility to contaminants) and to compensate for the no less obvious disadvantages (low conversion per cycle and low selectivity). DMTM was

recommended as a part of an integral energochemical process that combines production of methanol with generation of electric power.[185] This provides yet another benefit and allows maximum simplification of the technology and cut of the production cost of methanol with simultaneous reduction of specific emission of NO_x in the generation of electric power from natural gas.

Partial oxidation of methane homologues is studied in less detail. The oxidation of ethane and methane – ethane mixtures in a flow reactor at 10 – 70 atm was studied with variable macrokinetic parameters.[186, 187] The use of ethane and ethane-containing gases for direct gas-phase oxidation is in every respect more advantageous than the oxidation of methane-containing gases. Although this reaction yields similar major products (except for appearance of noticeable amounts of ethylene), their yields and the degree of conversion of the hydrocarbon gas are somewhat higher, while the working pressure and temperature are significantly lower than in methane oxidation. The increase in the yields of such valuable compounds as formaldehyde and ethanol is especially pronounced, although methanol remains to be the main oxidation liquid product. High total yields of oxygenates were achieved at relatively low pressures ($\sim$30 atm). The content of formaldehyde in liquid products was $\sim$30% at the total alcohol content of 45% and the methanol : ethanol ratio of 5 : 1. Such a ratio is characteristic of fuel alcohol mixtures that can directly be used as high-octane additives to motor fuels. This allows the direct gas-phase oxidation of ethane to be considered as a potential one-step procedure for production of formaldehyde and fuel alcohols. A promoting effect of methane on the formation of methanol and the yield of liquid products in the ethane oxidation was established. Presumably, this is due to the ability of methyl peroxide radicals generated upon methane oxidation to serve as effective branching species, whereas peroxide radicals generated in the oxidation of ethane and higher hydrocarbons can decompose by alternative routes that yield alkenes but do not result in branching.

Experimental studies and kinetic simulation of conversions of methane and ethane in their combined partial oxidation and of conversions of hydrocarbons C_1-C_4 in the oxidation of more complex mixtures imitating natural and associated gases have been carried out.[188] Under conditions of partial oxidation of hydrocarbons C_1-C_4 to oxygenates, fast burn-out of higher hydrocarbons at the initial O_2 concentration of 4% – 16% is accompanied by an increase in methane concentration, particularly as a result of their oxidative reforming. However, complete conversion of only one of these hydrocarbons in the oxidation of methane – ethane mixtures is impossible in principle, since both are oxidative interconversion products. The changes in the relative concentrations of hydrocarbons upon combined oxidation depend critically on the initial concentration of oxygen in the mixture. At the same time, the effect of temperature is far less pronounced, while the changes in the pressure in the range 25 – 70 atm have virtually no effect on this parameter.

Short-term catalytic impact on these complex non-linear systems that are far from the thermodynamic equilibrium as a means of the control over the chemical process is a promising trend in the study of partial oxidation of methane and its homologues. The nonlinear, in principle, nature of such systems determined by interconversions of numerous intermediates allows control over the evolution of the system and its transitions into different steady states by applying relatively weak impacts on the system.[189] However, these studies should be based on the use of reliable quantitative kinetic models of relevant homogeneous – heterogeneous processes. The development of such models is a very complicated task if we take into consideration the ambiguity of many kinetic parameters of even key elementary steps.

2. Homogeneous promotion of methane oxidation to oxygenates

Attempts to increase the yields of methane partial oxidation products by homogeneous promotion or using heterogeneous catalysis have been undertaken since the 1920's. Hydrogen peroxide and nitrogen oxides formerly employed in various industrial processes still remain the most popular homogeneous promoters. In the majority of cases, the effects of promoters are apparently confined to the decrease in either the temperature of the process or the induction period, but the yields of the reaction products are unaffected. Presumably,[190, 191] the failure to increase the product yields by promoting the reaction is due largely to the necessity of additional generation of radicals at very high rates comparable to those attainable in homogeneous branched-chain processes. Kinetic simulation showed that promotion of partial oxidation of methane can, in principle, significantly affect the yields of target products. For example, it is expected that the yield of formaldehyde can be increased by nearly an order of magnitude upon promotion of the oxidation of a $CH_4 : O_2 = 9 : 1$ mixture (1 atm, $T = 753$ K). However, this can be the case provided the promoter ensures the rate of the radical generation more than five orders of magnitude larger than that of their thermal generation in the reaction itself.[8, 189, 190]

The possibility of promoting the DMTM process with different radicals and molecules has been studied experimentally.[192] The concentrations of radicals above 0.1% could not be achieved irrespective of the nature of the radicals, since they readily interconverted in the gaseous phase. The introduction of radicals or $\sim$2% of different molecular promoters reduced the ignition delay without any effect on the yields of the reaction products. Among molecular compounds tested, the ability of H_2O_2 to reduce the ignition delay was the highest and exceeded twofold that of methanol.

The promotion of incomplete methane oxidation by nitrogen oxides can be concomitant with the catalysis of the formation of various oxygen-containing species. One of the pioneering studies in this field has demonstrated [193] that the addition of 2% NO to a $CH_4 : O_2 = 9 : 1$ mixture (1 atm, 560 °C) increased 10-fold the yield of formaldehyde (from 0.35% to 3.96%). Although this increase could be explained by the promoting effect of NO, it was assumed that it was a manifestation of homogeneous catalysis, since the reaction products contained no N_2O and only trace amounts of N_2.

The effect of nitric acid vapour ($\sim$0.26%) as a potential source of NO_2 on methane oxidation has been studied.[194] The addition of HNO_3 increased not only the degree of methane conversion, but also the general selectivity and the yields of organic products (from 0.7 to > 2%), mainly due to the formation of CH_3NO_2. In the presence of HNO_3 and at similar degrees of methane conversion, the selectivity towards CH_3 OH and HCHO changed only insignificantly, while the general selectivity and the yields of oxygenates increased due to the presence of CH_3NO_2. The selectivity towards HCHO and CH_3NO_2 increased with the increase in the degree of methane conversion in the presence of HNO_3, while the selectivity towards CH_3OH decreased under these conditions. It was assumed [194] that the effect of NO_2 is not confined to initiation alone, since the initial reaction temperature ($\sim$410 °C) was the same in all experiments with the same oxygen concentration (2.6%). No nitrogen was formed under these conditions, while the major part of NO_2 (40% – 80%) was converted into CH_3NO_2. In the authors opinion, NO_2 can be used as a catalyst in partial oxidation of methane provided that the conditions of this reaction or its individual steps favour the conversion of CH_3NO_2 into other oxygenates and regeneration of NO_2.

The effect of nitrogen oxides on partial oxidation of other lower alkanes is similar. In the gas-phase oxidation of CH_4, C_2H_6, C_3H_8 and iso-C_4H_{10}, the introduction of nitrogen oxides not only increased the rates of alkane conversions and reduced the initial temperature of the overall reaction, but also increased considerably the yields of the oxygenates, *i.e.*, aldehydes, ketones and alcohols.[195, 196] The experiments were carried out in a quartz reactor with an internal diameter of 8 mm; the flow rate was 120 ml min^{-1}; the partial pressures of alkanes, O_2 and NO were

5–10, 2.5–15 and 0.5–4 kPa, respectively.[195] The reaction mixture was diluted with helium to the total pressure of 101 kPa. After addition of NO, the oxidation of ethane and propane occurred at 400 °C, *i.e.,* at 100 °C lower temperature than in the absence of NO, while the activation energies of the reactions were equal to 208 (methane), 138 (ethane) (361 in the absence of NO) and 107 (propane) kJ mol^{-1} (275 in the absence of NO). The total yields of oxygenates under optimum conditions were as follows: 6.7% (methane), 11.3% (ethane), 12.9% (propane) and 28.7% (isobutane). Only trace amounts of nitroalkanes and N_2 were formed under these conditions. Thus, the bulk of added NO remained in the gas phase, which favoured its subsequent isolation and reuse as a catalyst for the oxidation of lower alkanes. The reaction between NO and alkanes did not occur in the absence of O_2, which points to the involvement of NO_2 in the oxidation and poses a question of the role of nitroalkanes as intermediates in this process. The latter were formed in small amounts in the oxidation carried out at low temperatures. However, direct studies of decomposition of nitropropane $C_3H_7NO_2$ established that C_3H_8 was formed as the main product, *i.e.*, nitroalkanes are not precursors of oxygenate. Contrariwise, the decomposition of iso-C_4H_9ONO at 400 °C resulted in the formation of acetone as the main product. The addition of a $NO-O_2$ mixture to the nitroalkane did not change the rate of acetone formation, but yielded HCOH, CO, CO_2 and CH_3NO_2 instead of soot. Thus, alkyl nitrite can serve as the oxygenate precursor.

It was suggested[196] that the oxidation of alkanes RH is catalysed by nitrogen oxides and involves the following main reactions:

$$2\,NO + O_2 \rightleftharpoons 2\,NO_2,$$

$$RH + NO_2 \longrightarrow R + HNO_2,$$

$$R + NO_2 \longrightarrow RONO,$$

$$R + NO_2 \longrightarrow RNO_2,$$

$$R + O_2 \longrightarrow RO_2,$$

$$RONO \longrightarrow R'CHO + R''(H) + NO;$$

in particular, at $R = CH_3$

$$CH_3ONO \longrightarrow HCHO + H + NO,$$

whereas at R = iso-C_4H_9

$$\text{iso-}C_4H_9ONO \longrightarrow CH_3COCH_3 + CH_3 + NO.$$

NO and NO_2 play the role of homogeneous catalysts, since the nitroalkanes formed fully decomposed at temperatures above 600 °C with simultaneous release of NO_x.

It should be taken into account that both hydrocarbons themselves and CO strongly promote oxidation of NO to NO_2 even at relatively low temperatures (300 °C). In addition, NO markedly accelerates the oxidation of methanol and ethanol formed, presumably *via* partially oxidised intermediates that are unstable under other conditions.[197]

A simplified system for the reaction of CH_4 with NO_x (in the absence of O_2) was analysed theoretically and the activation energies and rate constants for the reactions of nitrogen oxides with methane were calculated.[198] The activation energy of the reaction:

$$CH_4 + NO \longrightarrow CH_3 + HNO$$

is 65.6 kcal mol^{-1}, *i.e.*, higher than the activation energy (59.0 kcal mol^{-1}) of the reaction:

$$CH_4 + O_2 \longrightarrow CH_3 + HO_2.$$

This implies that NO cannot play the role of a promoter in this reaction. Contrariwise, the activation energy of the reaction

$$CH_4 + NO_2 \longrightarrow CH_3 + HNO_2$$

is equal to 37.6 kcal mol^{-1}, *i.e.*, it is this reaction that is presumably the promotor in the process. It is believed[198] that in the presence of oxygen this reaction is accompanied by fast conversion:

$$HNO_2 + O_2 \longrightarrow HO_2 + NO_2,$$

with the liberation of NO_2.

Since the formation of C_1-oxygenates proceeds *via* CH_3O as an intermediate, these may be formed at ~800 K because the energy barriers of all steps are below 40 kcal mol^{-1}. In terms of the hypothetical mechanism, the increase in NO concentration favours a higher yield of CH_2O with a corresponding decrease in the yield of CH_3OH, which is consistent with the above-mentioned data for the CH_4-O_2-NO system.

Somewhat unexpected results have been reported concerning the effects of nitrogen oxides on incomplete oxidation of methane.[199,200] The experimental conditions were similar to those described.[195,196] In the majority of cases, reaction mixtures contained 55.6% CH_4, 27.7% O_2, 0.5% NO_x and 16.2% He. The reaction was carried out in a quartz reactor with an internal diameter 7 mm and the length of 200 mm at 1 atm, ~800 K and a space velocity of 120 ml min^{-1}. The product yields were determined at the same degree of methane conversion (10%). Under these conditions, the reaction of CH_4 with NO_2 in the absence of oxygen yielded predominantly formaldehyde, whereas the reaction with NO yielded no oxidation products at all. The introduction of NO_x to the system CH_4-O_2 enabled high selectivity towards formaldehyde (24.5%) and even higher selectivity towards methanol (27.3%), although in all previous studies no methanol was formed at all or it was formed in only trace amounts. Nitromethane CH_3NO_2 was isolated together with methanol and formaldehyde and its final concentration correlated quantitatively with the initial concentration of added nitrogen oxides.

The effects of various parameters on the temperature of partial oxidation of methane and the product yields have been studied.[199–201] At 0.1 and 5 MPa, the increase in the initial concentration of NO to 1% caused a significant (by ~100 K) reduction of the reaction temperature, although the maximum degree of methane conversion did not change. However, further increase (up to 1.5%) of NO concentration had no effect. At the indicated pressure, the selectivity towards oxygenates (methanol, formaldehyde, nitromethane) reached a maximum at [NO] ≈ 0.5%, which is considered as the optimum concentration. The selectivity towards ethane dropped down quickly to a nearly zero level with the increase in the NO concentration. Dilution of the reaction mixture with helium, at least to the concentration of 60%, had little effect. Even the dependence of the product yields on such a critical parameter as the $CH_4:O_2$ ratio shows that the yields of methanol and formaldehyde did not change appreciably with the increase in this ratio to 10 despite the presence of a maximum around $CH_4:O_2 = 2$. At $CH_4:O_2 < 2$, the yield of methanol decreased with a concomitant increase in the yield of formaldehyde. However, neither the increase in the space velocity (from 1000 to 4000 h^{-1}), nor the addition of water (up to 16%) had any pronounced effect on the yields of oxygenates. On the whole, NO_2 exerted approximately the same effect as NO.

The consistently high yields of methanol (and nitromethane) in a broad range of experimental conditions call into question the arguments put forward by Suzuki *et al.*[199–201] as a plausible reason for the considerable discrepancies between their experimental results and those obtained under virtually identical conditions.[195,196] Since these works differ from one another by a large number of parameters, the actual dependence of the product yields on reaction conditions is impossible to establish without the use of kinetic simulation.

As for the mechanism of this reaction, it was suggested[199,200] that the interaction of methane with NO_2 not only favours the generation of radicals, but the nitrogen oxides formed thereupon

promote the formation of an alkoxy radical as the oxygenate precursor:

$$CH_3 + NO_2 \longrightarrow CH_3O + NO,$$

$$CH_3O_2 + NO \longrightarrow CH_3O + NO_2.$$

Supporting evidence in favour of these experimental results [199–201] was obtained in the simulation of NO_x-promoted oxidation of methane using a CHEMKIN III software.[202]

It is noteworthy that the beneficial effect of NO_x promotion is manifested exclusively at low pressures, whereas at pressures above 1 MPa this effect is less pronounced.[201] Thus at 1 MPa, the decrease in the reaction temperature at 4% methane conversion did not exceed 25 K. The selectivity towards oxygenates did not depend on NO_x concentration, while the selectivity towards methanol in the absence of NO_x amounted to 30%. This suggests that promotion makes no sense at pressures above 1 MPa. This is consistent with the hypothesis according to which the role of promotion in this reaction becomes insignificant when the oxidation process goes to the branched-chain regime with an increase in pressure.[8] This circumstance notwithstanding, the catalytic effect of NO_x on oxygenate formation at high pressures is likely. The same group of investigators [203] demonstrated the possibility of a slight increase in the yield of methanol in the system CH_4-O_2-NO ($T = 550$ °C, $P = 0.4$ MPa) due to a virtually complete conversion of formaldehyde upon introduction of a catalyst ($Cu-ZnO/SiO_2$).[203]

Partial oxidation of methane upon combined use of nitrogen(I) oxide and a heterogeneous catalyst has been described.[204] In such reactions, the catalyst usually fulfils several functions: not only does it induce the generation of radicals and catalyse the formation of the reaction products, but it also favours their subsequent decomposition. Separation of these functions was effected with NO as a radical promoter, subsequent reaction was carried out over V_2O_5/SiO_2 with small specific surface (~ 1 m^2 g^{-1}). Low decomposition rates of the partial oxidation products over this catalyst enabled a much higher yield (7%) of the C_1 oxygenates (methanol and formaldehyde) than over catalysts with well-developed surfaces. In more recent studies,[205] the total yields of oxygenates were even higher (up to 16%), which can be considered as the maximum level currently attainable.

Although in the majority of studies devoted to the promotion of methane oxidation by nitrogen oxides at atmospheric pressure, the total yields of oxygenates did not exceed 4%–7%, it was reported [206] that their yields were 11% upon methane oxidation, 16% upon methane oxidation in the presence of trace amounts (0.7%) of ethane and 24% upon ethane oxidation. However, in contrast to the studies [204, 205] where methanol was formed as the main product, in the latter case it was formaldehyde that was virtually exclusively formed.

3. Physical methods for promoting oxidative conversions of lower alkanes

Oxidative processes are promoted not only by chemical, but also by physical methods, in the first place, by electric discharge, plasma and molecular beams. Gas-discharge plasma is widely used for the initiation of chemical reactions, which can be exemplified by direct conversion of methane into acetylene upon thermal arc discharge. This method developed 50 years ago is also employed for the production of H_2. The possibility of applying non-equilibrium plasma to low-temperature conversion of methane into synthesis gas, oxygenates and higher hydrocarbons is under intensive study. The creation of non-equilibrium plasma is an effective approach to promoting chemical reactions due to interaction of electrons and ions accelerated in the electric field with molecules and radicals. In contrast to heterogeneous catalysis, such a promotion occurs in the bulk of the reactor. Plasma is generated using different kinds of electric discharges, *e.g.*, corona, electric arc, barrier, glow, microwave, pulsed, *etc*. In some studies, this technique was used in combination with heterogeneous catalysis. Taking into account the tremendous number of investigations in this area, here we shall confine ourselves to the consideration of only some of the most recent studies.

Corona discharge was successfully employed for efficient preparation of synthesis gas and C_2 hydrocarbons from methane and air.[207] The effects of various parameters (*e.g.*, $CH_4:O_2$ ratio, addition of ethane, dilution with inert gases, residence time, power and frequency of the discharge, the pulse form) on the reaction rate were investigated. The conversion of methane and of oxygen increased with an increase in the discharge power, but decreased with the increase in the $CH_4:O_2$ ratio, flow rate and interval between the pulses. In the absence of oxygen, the degree of methane conversion did not exceed 3%, *i.e.*, under these conditions, as in the case of the barrier discharge, methane did not undergo any conversions. This is apparently associated with the low average electron energy of the barrier discharge equal to 5 eV, which is sufficient for the formation of negative oxygen ions, but insufficient for the activation of methane having the ionisation potential of > 12 eV. Negative oxygen ions activate methane, likely owing to abstraction of hydrogen atoms and formation of methyl radicals. Hydrogen and ethane are formed as a result of discharge-induced conversion of pure methane. The minimum energy required for the conversion in a methane–air system at the optimum discharge frequency of 300 Hz is 21 eV per carbon atom.

The selectivity towards ethane upon discharge-induced oxidative methane dimerisation was inversely proportional to methane conversion; subsequent dehydrogenation of ethane yielded ethylene and acetylene. The degree of discharge-induced conversion of ethane added to the reaction mixture is more than fivefold larger than that of methane due to the lower activation energy for hydrogen abstraction from this molecule.[207]

The addition of water vapour significantly enhanced the conversion of methane and oxygen and increased the efficiency in energy at low O_2 content. At a $CH_4:O_2$ ratio of 5:1, the increase in the concentration of water vapour from 0% to 50% reduced power consumption per methane molecule in the corona discharge from 68 to 13 eV. The percentage of the reaction products showed a stronger dependence on the composition of the gas mixture than on the discharge power or frequency.[208]

Joint conversion of two essential greenhouse gases, *viz*., CH_4 and CO_2, *e.g.*, by dimerisation of methane in the presence of CO_2, is a promising trend in plasmochemistry. This problem has been documented in numerous publications. Thus the use of pulsed microwave discharges in a flow of the reactants $CH_4:CO_2 = 1.5:1$ (200 ml min^{-1}) at ambient pressure and the microwave amplitude of 120 W enabled virtually equal (70%) degrees of conversion of CH_4 and CO_2 with the selectivities in CO, C_2H_2 and C_2H_4 of 75%, 17.8% and 4.1%, respectively.[209] The $H_2:CO$ ratio in the reaction products was 1.5.

Joint conversion of CH_4 and CO_2 into synthesis gas as well as methane conversion into acetylene was carried out using different types of pulse discharge.[210] The reactions were performed at atmospheric pressure in the absence of catalysts. The analysis of the reaction products and selectivities of their formation revealed that the chemical features of the processes varied widely depending on the discharge type. The compositions and ratios of the compounds formed in the methane plasma depended critically on the pulse energy. C_2H_6 was almost exclusively formed at low energies, as the energy increased, the reaction products contained also C_2H_4 and C_2H_2, while at high energies C_2H_2 became the predominant and then the only plasmochemical reaction product.

The low temperature of the process, lack of thermodynamic restrictions and possibility of achieving the required $H_2:CO$ ratios by simply varying the $CH_4:CO_2$ ratio in the original mixture, are the attractive features for the production of synthesis gas by CH_4 and CO_2 conversion in non-equilibrium plasma. The $H_2:CO$ ratio is virtually independent of the reactor temperature or the specific power of the electric discharge. The maximum degree of conversion of CH_4 and CO_2 ($> 70\%$ and $> 60\%$,

respectively) was reached at the specific energy of the discharge of 60–70 kJ litre^{-1}. This value obtained in the electrode discharge [210] was much lower than that in the dielectric barrier discharge, which was probably less efficient in the conversion of electrical energy into chemical energy. Nevertheless, low efficiency of this conversion (nearly two orders of magnitude lower than in the thermal arc discharge) is the main obstacle to the practical application of non-equilibrium plasma for conversion and reforming of methane.

The potential of different devices making use of gas discharge (plasmotrons) in the production of synthesis gas in combined oxidative-steam reforming of methane was compared with that of thermal processes.[211] Although the use of plasmotrons enables a nearly complete conversion of methane at relatively low temperatures (820–900 K) and much lower capital investments ($\sim$65 per 1 m^3 H_2 per hour) in comparison with processes conducted in chemical reactors (750–900 per 1 m^3 H_2 per hour), the overall economic assessments are not in favour of plasmochemical technologies. The cost of hydrogen exceeds that produced in conventional reactors 3–5-fold. Therefore, such attractive features of plasmochemical reactors as simple and compact design and low cost can only find application in the design of small-sized units, *e.g.*, for hydrogen fuel cells in motor vehicles.

Direct conversion of methane into C_2 hydrocarbons was studied in cold plasma in the presence of catalysts at 20 °C and at ambient pressure.[212] The effects of such factors as the reactor shape, input power, flow rate, the N_2 : CH_4 ratio and catalyst type, on the selectivity towards these hydrocarbons were investigated. The selectivity was above 98% at a methane conversion of up to 60%, *i.e.*, the yields of these hydrocarbons exceeded 50%. V_2O_5 manifested the highest efficiency among the catalysts assayed. Since the ordinary catalysts of oxidative dimerisation of methane did not manifest any activity in the plasmochemical process, the role of a catalyst under cold plasma conditions was considered to differ from that in oxidative dimerisation.[212] This consists of fast recombination of radicals generated in the plasma and rapid desorption of H_2 and C_2 hydrocarbons from the surface, which likely prevents the formation of higher hydrocarbons. The combined effect of microwave irradiation and a catalyst on the conversions of methane into hydrogen, synthesis gas, acetylene and carbon has been studied [213] with special reference to direct microwave excitation of separate grains of the catalyst and electric discharge in the gas near the catalyst surface.

The majority of approaches to the conversion of hydrocarbons by plasmochemical methods envisage, in one way or another, the attainment of equilibrium concentrations of the reaction products, at least in the discharge zone. However, due to the non-selectivity of the discharge action (and often due to multiple cleavage and recombination of the same bonds), the transformation of even one molecule requires very high energy that exceeds significantly that of the chemical bonds that undergo transformations. Taking into account the real efficiency factor of transformation of the primary energy into the high-potential discharge energy, the energetic and, as a consequence, the economic value of the matter remains inadmissibly high. The use of plasmochemical methods for potent promoting effects on non-equilibrium chemical systems, *e.g.*, branched-chain processes including those coupled with heterogeneous catalysis, seems to hold much more promise in this respect. Here one can expect significant changes in the chemical behaviour of systems upon relatively weak energetic impact.

4. Catalytic oxidation of methane to methanol

Both heterogeneous-catalytic and homogeneous oxidation of methane to methanol have been the subject of active investigations over the past 100 years. Studies by Nalbandyan, Mukhlenov, Gomonaya *et al.* (for details see Ref. 8) demonstrated high selectivity of these reactions (which in some cases amounted 100%!), attained however at low degrees of conversion. Methanol and formaldehyde formed in yields >3%–4% under conditions of essentially heterogeneous mechanism of the process. Our studies have shown [190, 191] that the generation of methyl radicals in the presence of catalysts is a characteristic feature of mechanisms of catalytic oxidation of methane to methanol, formaldehyde and ethylene. Their subsequent conversions in the gas phase or over the surface yield the reaction products. The highest yields of CH_3OH and CH_2O were 2%–4% and those of C_2 hydrocarbons were $\sim$25%. A scheme of radical-chain oxidation of methane was proposed to rationalise these yields.[8, 190, 191]

The so-called reductive activation where the oxidation is carried out by an $H_2 + O_2$ mixture or H_2O_2 is a novel procedure for converting methane to methanol. Apparently, the oxidation involves the OH radicals generated. The selectivity towards methanol formed from the $CH_4 + O_2 + H_2$ mixture over $Fe_{0.5}Al_{1.5}O_3$ at >330 °C and atmospheric pressure was 28% at the degree of conversion of 0.4%–1.5%.[214] The IR spectra recorded over the catalyst surface *in situ* manifested the presence of peroxide adsorption bands at 895 cm^{-1}. In the absence of hydrogen, formaldehyde was formed at $T > 530$ °C in small amounts. It is suggested that the role of the active site is played by the Fe(III) ion with tetrahedral coordination:

$$O_2^- Fe + CH_4 \rightleftharpoons CH_3-O-Fe + OH^-,$$

$$CH_3-O-Fe + OH^- \longrightarrow CH_3OH + FeO^-.$$

Iron derivatives were found to be the most selective catalysts in the partial oxidation of methane to methanol. The selectivity towards CH_2O over $FePO_4$ (2%–16%) supported over Al_2O_3, ZrO_2 and TiO_2 reached 63% at low degrees of conversion; the reaction over $FePO_4/SiO_2$ gave additionally CH_3OH.[215] In the authors opinion, the high selectivity of this catalyst can be attributed to the formation of pentacoordinate Fe as can be evidenced from the pattern of the Mössbauer spectra.

Iron molybdate over a mesoporous support (MSM-41) was more selective in the oxidation of methane by N_2O in CH_2O and CH_3OH (300–500 °C) than non-supported $FePO_4$ (see Ref. 216). The oxidation of methane by oxygen proceeded with 60% selectivity and afforded CH_2O and CO (yields 1%–2%). The selectivity towards CH_3OH and CO_2 increased when N_2O was used instead of O_2 in the oxidation of methane over V_2O_5.[217]

In a series of investigations,[218–220] the oxidation of methane to methanol was carried out over Pd powder dissolved in oleum. The yield of methanol reached 20%. The following reactions took place:

$$Pd^{2+} + CH_4 \rightleftharpoons Pd^{2+}-CH_3^- + H^+,$$

$$Pd^{2+}-CH_3^- + H_2SO_4 \longrightarrow CH_3SO_3H + Pd^0 + H^+,$$

$$Pd^0 + SO_3 \longrightarrow Pd^{2+} + SO_2 + O^{2-}.$$

The oxidation of methane to methanol with a $H_2SO_4 + SO_3$ mixture in the presence of mercury salts was carried out at 150–200 °C and at CH_4 pressures of 4–10 MPa; the yields were up to 39%.[221] The yield of methanol increased with the increase in both pressure and temperature.

The yield of CH_3OH in the oxidation of a $CH_4 + O_2 + NO$ mixture also increased in the presence of $Cu-ZnO/Al_2O_3$.[222] This process involved several reactions: 1) formation of CH_3OH from CH_2O and H_2; 2) conversion of water gas at 350 °C and higher temperatures; 3) selective oxidation of methane with an $O_2 + NO$ mixture at 550 °C. At 5.5% conversion, the selectivity towards CH_3OH was 39%.

In addition to the ongoing studies into the mechanism of this reaction, the possibility of increasing the yields of methanol and other oxygenates is being studied under various reaction conditions. Two of the most obvious trends include the maintenance of constant (or quasi-constant) low concentrations of oxygen in the course of the reaction and continuous or periodic elimination of the target products from the reaction zone (or their binding).

The feasibility of countercurrent adsorption of the reaction products was studied under laboratory conditions using the so-

called Simulated Countercurrent Moving Bed Chromatographic Reactor (SCMCR) previously developed for the oxidative dimerisation of methane.[223] This method has been used for the isolation of methanol in the partial homogeneous oxidation of methane.[181] The nonconsumed methane was separated from the reaction products by consecutive cyclic switching of the gas flow from the homogeneous reactor to one of the three parallel chromatographic columns filled with an adsorbent. Then the column was blown with helium and desorbed methane and carbon oxides were injected into the reactor. After that, liquid products (methanol and water) were collected from the reactor outlet. To a certain extent, such a system simulated the operation of a reactor with a countercurrent adsorbent, its substantial difference being that the optimisation of oxidation and adsorption–desorption was performed under different conditions and the choice of the adsorbent was arbitrary. A typical adsorbent for such a system is, *e.g.*, Supelcoport (80/100 mesh) impregnated with 10% (w/w) Carbowax. However, direct extrapolation of this technology to industrial conditions is hardly justified due to its complexity and vast expenditure of the purge gas. Nevertheless, it presents interest as an illustration of combined application of DMTM and adsorptive methods. Under optimum conditions (P = 10 MPa, T = 477 °C, $CH_4 : O_2$ = 16.3), the selectivity towards methanol in this cyclic process was 50% at 50% conversion, which corresponds to 25% yield of methanol.

Studies of 'α-sites' of Fe-containing zeolites that can be involved in methane activation are currently underway.[224–227] According to data from Mössbauer spectroscopy, such a site consists of oxygen (the so-called α-oxygen) bound to two Fe atoms. Such an active site effects the catalytic oxidation of benzene into phenol by N_2O. Zeolite Fe–ZSM-5 manifests higher reactivity in comparison with Fe-mordenite, Fe-chabazite and Fe–CIT-5. It was found that α-sites are formed upon thermal activation of the zeolite and their formation involves Fe atoms protruding from the lattice. Presumably, they are localised in the intersection points of zeolite Fe–ZSM-5 channels and their maximum concentration is virtually the same as that of the intersection points of zeolite channels ($\sim 10^{19}$ g^{-1}). The properties of α-sites are similar to those of the free-radical species O^-.

The reaction of methane with the α-sites of Fe-containing zeolites yields methanol:

$$CH_4 + O_{ads} \longrightarrow (CH_3OH)_{ads},$$

and occurs at a very fast rate even at −30 °C, but is not catalytic. Heating causes decomposition of methanol and release of CO and H_2 into the gas phase. Methane reacts with α-oxygen in a stoichiometric ratio 1 : 1.8. Heating of the zeolite results in the release of the excess oxygen in the form of O_2.

Kinetic simulation of the hydroxylation of methane to methanol under the action of methane monooxygenase and Fe-containing complexes has been carried out.[228] The activation proceeded *via* pentacoordinate carbon. Binuclear sites Fe(III)–O–Fe(III) played the role of active sites.

In summary, it may be said that novel promising catalytic reactions have recently been developed for the oxidation of methane to methanol, particularly, with the involvement of alternative oxidants (N_2O, H_2O_2, $H_2 + O_2$). Many of these reactions are catalysed by Fe-containing oxides or zeolites. The highest yields (up to 40%–50%) are achieved in a liquid-phase procedure developed by Catalytica Ltd. for the oxidation of methane to methanol. In this procedure, Hg, Pt and Pd salts are used as catalysts and concentrated H_2SO_4 is used as an oxidant.[218]

5. Catalytic oxidation of methane to formaldehyde

Similar to the oxidation of methane to methanol, the yields in the oxidation of methane to formaldehyde pass through a maximum that amounts to 2%–4%. In our studies,[190, 191] the existence of maximum yields was interpreted in terms of a heterogeneous–homogeneous mechanism that involves the intermediate formation of methyl radicals released into the gas phase. The selectivity of this reaction at low (~2%) degrees of conversion may reach 100%.

Selective (or relatively selective) catalysts usually contain oxide forms of several elements, *e.g.,* V, Si, Mo and Fe. The addition of a minor amount of Co enhances the activity and selectivity of partial oxidation, but a large amount brings about deep oxidation of methane. The analysis of IR spectra recorded in the interaction of oxidised surfaces MoO_3(100) and MoO_3(110) with methane revealed the formation of CH_3O groups;[229] their decomposition yielded the radicals CH_3.

The reactions of methyl radicals generated upon decomposition of azomethane over V_2O_5/SiO_2, which affords high yields of formaldehyde, were used to study the heterogeneous–homogeneous mechanism of partial oxidation of methane to oxygenates.[213] The formation of CH_3O^- groups upon introduction of the CH_3 radicals was established by IR spectroscopy. According to EPR data, under these conditions V^{5+} is reduced to V^{4+}. The CH_3O groups can further be converted into CH_2O or react with H_2O to give CH_3OH. The formation of methanol at 300 °C and of formaldehyde at 400 °C over V_2O_5/SiO_2 (*i.e.*, at lower temperatures than over V_2O_5) suggests possible involvement of the interactions of CH_3O^- with water or surface OH groups, which increases the yields of CH_3OH. Thus, the main reactions are as follows:

$$CH_3 + M^{(n+1)+}O^{2-} \longrightarrow M^{n+}(OCH_3)^-(S) \longrightarrow$$
$$\longrightarrow M^{(n+1)+}O^{2-} + CH_2O,$$
$$CH_3OH \underset{H^+}{\overset{-H^+}{\rightleftharpoons}} CH_3O^-(S) \longrightarrow CH_2O + OH^-(S).$$

The oxidation of methane to formaldehyde over SiO_2 and V_2O_5/SiO_2 has been studied.[230–236] The yield of CH_2O over SiO_2 was increased to 15%–25% where the reaction was carried out in a recycling system at 650–690 °C. In the authors's opinion,[232] the oxidation to CH_2O occurred due to the presence of reduced sites on SiO_2. The 5% V_2O_5/SiO_2 catalyst exceeded pure SiO_2 in activity, but was less selective. The yield of CH_2O over this catalyst was 16.1%–24.6% at 670 °C, the selectivity was 30.1%–56%, while the efficiency was 240 g per kg of the catalyst per hour. No deactivation of the catalyst was observed over 3000 h.

The mechanism of partial oxidation of methane to formaldehyde over the same catalyst (V_2O_5/SiO_2) was studied *in situ* using Raman spectroscopy.[237, 238] At low concentrations of V_2O_5, the activity of the catalyst increased linearly with the increase in vanadium content. This suggests that the role of active sites is played by isolated V^{5+} ions. The Raman spectra recorded after the termination of the reaction demonstrated that no reduction of vanadium took place. The stability of V^{5+} is the main reason for the high selectivity towards CH_2O. The unique properties of SiO_2 as a support were attributed to its low acidity, which favours deep oxidation.

The oxidation of methane to formaldehyde over V_2O_5/SiO_2 was studied in a recycling reactor at 570–630 °C with freezing-out. At the degree of conversion of CH_4 of 89%, the selectivity remained at the level of 56%, and the yield of CH_2O amounted to ~50%. Without recycling, the yield was 2% in a single run.

The oxidation of methane to the oxygenates CH_2O and CH_3OH in the presence of water vapour was studied at 600 °C using MoO_3/SiO_2 as a catalyst.[239] The increase in water vapour pressure enhanced the selectivity towards oxygenates, while the selectivity towards CO and CO_2 decreased. This was attributed to the formation of silicomolybdic acid ($H_4SiMo_{12}O_{40}$) on the surface of SiO_2 (IR spectroscopic data). In the absence of water vapour, the acid is decomposed at 600 °C. In the presence of 60% H_2O, the conversion of CH_4 was 25%, while the selectivity towards the target products was as high as 90%. Stable conversion of methane lasted 350 h at the optimum value of the $P_{CH_4} : P_{O_2} = 3 : 2$ ratio.

A comparison of the catalytic properties of Mo–ZSM-5 (0.3%–3.0% Mo) and H–ZSM-5 revealed[240] that the former

was more reactive, while the latter was more selective in the oxidation of CH_4 to CH_2O. At 600 °C, the selectivity towards formaldehyde over Mo–ZSM-5 was 10.6% at the 6.5% conversion of CH_4.

SiO_2-supported molybdates of various metals were used as catalysts in this reaction.[241] Rb_2MoO_4/SiO_2 manifested the highest activity at 580–660 °C. CO, H_2, CH_2O, C_2H_6 and CO_2 were produced over this catalyst. The maximum amount of CH_2O was formed over MoO_3/SiO_2. Thus at 550 °C the selectivity was 20%–30% at the conversion of 3%–5%. A mechanism was proposed implying the involvement of surface O^- sites and the reduction of Mo^{6+} to Mo^{5+}.

A relatively high yield of formaldehyde was obtained upon oxidation of methane over W–ZSM-5 (0.3%–11.9% W) at 650 °C.[242,243] The selectivity towards CH_2O reached 11.0% at the 51.2% conversion. The formation of WO_3 monomers, octahedral polymers and WO_3 crystals was obvserved on the surface of the catalyst. The W–ZSM-5 catalyst was more selective than MoO_3 and WO_3.

Partial oxidation of methane was also studied over zeolites containing no transition metals.[244] The oxidation of methane and ethane was carried out over Na–ZSM-5 and H–ZSM-5 at 670–700 °C in a system with CH_2O and CH_3OH freezing-out. The selectivity towards $CH_3OH + CH_2O$ reached 30% at the 4% conversion. The following oxidation scheme was proposed:

$$CH_4 \longrightarrow CH_3 \longrightarrow CH_3OO \longrightarrow CH_2O \longrightarrow CO + CO_2,$$

$$CH_3OO \longrightarrow CH_3OH \longrightarrow CH_2O \longrightarrow CO + CO_2.$$

The high efficiency of the H–ZSM-5 catalyst is due the high reactivity of the lattice oxygen as can be judged from the results of ^{18}O tracer experiments. Hydrogen binds to CH_2O on the catalyst surface to yield CH_3OH, while CH_2O is a direct dehydration product of CH_3OH. IR spectroscopic studies have shown [245] that the siloxane (Si–O–Si) bonds are involved in partial oxidation of CH_4 over SiO_2. Probably, these bonds are strained since no signals were observed in the EPR spectra.

Methyl formate can be prepared from methane by a two-step reaction over Al_2O_3, SiO_2, TiO_2, ZrO_2 and SO_4/ZrO_2.[246]

$$CH_4 + O_2 \longrightarrow CH_2O + H_2O,$$

$$2\,CH_2O \longrightarrow HCOOCH_3.$$

The maximum degree of conversion of CH_2O over ZrO_2 in the second step (170 °C) was 97% at the selectivity of 94%. The total yield of the reaction product over two steps was 7%–12%, which is one of the highest presently attainable in the oxidation of methane to oxygenates.

6. Production of formic acid

Reductive oxidation of the $CH_4 + O_2 + H_2$ mixture over a heteropolyacid catalyst $Pd_{0.08}Cs_{2.5}H_{0.34}PVMo_{11}O_{40}$ was proposed for the production of HCOOH from methane.[247] At 150–300 °C, the reaction rate reached 1.2×10^{-4} mol h^{-1} (g cat.)$^{-1}$, *i.e.,* it was 700 times higher than over the previously investigated $FePO_4$ catalyst. The conversion was 8% at 300 °C, while the selectivity towards formic acid was 60%. The addition of H_2O accelerated the reaction.

7. Production of acetic acid

A new method for the production of acetic acid from methane bypassing the formation of synthesis gas has been developed.[248] In the gas phase, methane undergoes direct oxidation to methanol which is further carbonylated over a supported catalyst.

$$CH_4 + \frac{1}{2}O_2 \longrightarrow CH_3OH,$$

$$CH_3OH + CO \longrightarrow CH_3CO_2H.$$

The conversion of methane per cycle was 6%–12%. Usually, oxygen was consumed totally at temperatures above 400 °C. The reaction was carried out at ~7 MPa. The water vapour formed is utilised for technological purposes. At the indicated pressure and temperatures (200–250 °C), methanol undergoes carbonylation over Pd/C in the presence of CH_3I to afford CH_3CO_2H and $CH_3CO_2CH_3$. The fact that the catalytic activity is retained over 600 h suggests that the carbonylation takes place in the gas phase. According to estimates, the production cost of acetic acid produced by this method is lower than in conventional procedures.

IV. Oxidative coupling of methane and related processes

1. Oxidative coupling of methane

Oxidative coupling of methane (OCM) resulting in C_2 hydrocarbons was discovered in the early 1980's. A great number of catalysts of this reaction have been investigated; more than 500 relevant papers are cited in the monograph.[8] The most reactive and selective catalysts afford C_2 hydrocarbons in up to 25% yield. The reaction kinetics were studied and the heterogeneous–homogeneous reaction mechanism, which is now universally acknowledged, was developed. However, in recent years the number of publications devoted to oxidative coupling of methane decreased substantially. The principal details of the reaction mechanism are now well established, but economic reasons obviate large-scale production of ethylene by this method.

a. Catalysts

The search for novel OCM catalysts is still in progress, but the yields of C_2 hydrocarbons have never exceeded the critical level of ~25%. Active catalysts usually contain oxides of alkaline-earth or rare-earth metals. The OCM reaction over substituted hydroxyapatite $Ca_{10-x}Pb_x(PO_4)_6(OH)_2$ ($x = 0.10$) was studied at 675–800 °C. This catalyst manifested the highest activity and higher thermal stability than non-substituted Pb-apatite. The maximum yield of C_2 hydrocarbons at 750 °C was 22%.

When OCM was carried out over the active catalyst SrO/La_2O_3 at 800–850 °C, the maximum conversion of methane was 30.1% at 85.6% selectivity.[249,250] Its catalytic properties were attributed to the basicity of the oxide.

The addition of Na to a 10% PrO_x/MgO catalyst decreased its activity in OCM, but sharply increased its selectivity.[251] At 750 °C, the conversion was 10.2%, while the selectivity reached 80.2%. The addition of SrF_3 and BaF_2 to Ln_2O_3 and LnOF (Ln stands for any rare-earth element) resulted in the enhancement of their activities.[252] Presumably, in this case the two phases interact with one another. At 800 °C, the highest yield (19%) was obtained over 50% SrF_2/Sm_2O_3: the conversion was 34%, the selectivity towards C_2 products was 55.8%. In the authors' opinion, [252] the O_2^- ion on LnOF is the active site in this reaction, as can be evidenced from the appearance of a band at 1090 cm^{-1} in the IR spectrum at 750 °C. Its intensity decreased upon interaction of the catalyst with CH_4.

The addition of Ce to Na/CaO resulted in an eightfold increase in its activity in OCM at 750 °C.[253] The role of active sites was played not only by Na^+O^-, but also by peroxides. Cerium oxide enhanced the regeneration of O^- and Na_2O_2 active sites.

$$Ce^{4+} + O_{ads}^{2-} \longrightarrow Ce^{3+} + O_{ads}^{-},$$

$$Ce^{3+} + \frac{1}{2}O_2 \longrightarrow Ce^{4+} + O_{ads}^{-}.$$

The selectivity towards C_2 products reached 80% at 10.5% conversion.

α-Al_2O_3 was found to be the best support for a Pb–Sn–O catalyst.[254,255] At 800 °C, the conversion of methane was 14.9%, the selectivity towards C_2H_6 was 35.7%, while that towards C_2H_4 was 15.7%.

Novel active catalysts were prepared from the superacids WO_3/ZrO_2 as supports.[256] The latter were impregnated with Eu or Ce together with Li_2CO_3 or with Ce or Mn together with NaCl. The former manifested long-lasting (100 h) albeit moderate activities (the yield of C_2 was 18%), while the latter manifested exceptionally high activity (the product yields were > 30%), but rapidly deactivated.

$Mn/Na_2WO_4/SiO_2$ was found to be one of the most active catalysts,[257] which retained stability for 97 h. $Mn/Na_2WO_4/MgO$ was less stable: its activity decreased gradually due to the presence of a hot spot. The hot spot temperature exceeded the temperatures in other parts of the layer by 150 °C. A series of novel efficient catalysts, *viz.*, SiO_2-supported $Mn(NO_3)_2$ and Y_2WO_4 or X_2MoO_4 (X = Li, Na, K, Rb, Cs; Y = K and Ca), were prepared.[258–260] The alkali oxide the decreased the quartz → α-cristobalite transition point, which is prerequisite for the preparation of active and stable catalysts. The active sites of the supported tungsten catalyst contained W–O clusters stabilised by alkalis. K/W/Mn and Rb/W/Mn were the systems of choice. In the authors' opinion,[260] the tetrahedral coordination of tungsten on the surface is a prerequisite for the manifestation of catalytic activity. The maximum yield of the C_2 products (29.0% at 66.6% selectivity) was achieved over $K_2WO_4 - Mn/SiO_2$ at 800 °C. At high temperatures, the Na_2WO_4/SiO_2 catalyst was also active in the absence of Mn.[261]

C_2 Hydrocarbons can be prepared from methane over MgO/C and Sm_2O_3/C catalysts in the presence of N_2O as an oxidant.[262] Without N_2O, the conversion of CH_4 at 850 °C was very low, while in its presence the conversion over MgO/C and Sm_2O_3/C reached 21.2% and 21.3%, respectively. The selectivity towards C_2H_6 in the presence of N_2O increased to 80% at 12% conversion. Hydroxyapatite was used as a catalyst in N_2O-assisted OCM.[263] At 700–750 °C, the selectivity towards the products reached 80% at 80% conversion of N_2O and at ~4% conversion of CH_4. At Mn : Si = 0.1, the selectivity towards C_2 was 88%, the yield was 4.5%.

A combination of MnO_x and $SrCO_3$ allows one to prepare a selective catalyst for OCM[264] with CO_2 as an oxidant. The activation of CO_2 and methane includes the electronic transitions $Mn^{2+} \rightleftharpoons Mn^{3+} + e^-$.

$$SrCO_3 \rightleftharpoons SrO + CO_{2\,ads},$$

$$CO_{2\,ads} + Mn^{2+} \longrightarrow CO + O^- + Mn^{3+},$$

$$O^- + 2\,CH_4 + Mn^{3+} \longrightarrow 2\,CH_3 + H_2O + Mn^{2+},$$

$$2\,CH_3 \longrightarrow C_2H_6.$$

b. Mechanism

The Lansford catalyst (Li/MgO) for OCM was studied by X-ray phase analysis, XPS, EXAFS and XANES (X-Rays Absorption Near Edge Structure).[265] At the concentration < 2.5%, lithium penetrated into the bulk of MgO as a result of which its crystallinity diminished. Defects in the near-surface layers of MgO and Li/MgO are detected after termination of the reaction. The Li/MgO catalyst manifested much higher activity in OCM than MgO.

Studies of OCM over Na_2O/CaO by conductivity and contact potential difference methods showed[266] that Na_2O induced appearance of anionic vacancies in the CaO lattice. These vacancies can be localised on the surface and thus decrease the selectivity towards C_2 products. Experiments with TAP reactors revealed[267] that enhanced activity of Na_2O/CaO in OCM reflected the low degree of saturation of its surface with oxygen. A kinetic scheme that takes into account only surface reactions was proposed.

The use of Raman spectroscopy for the study of oxidative coupling of methane over Nd_2O_3, BaO and BaX_2 (X = F, Cl, Br) revealed the presence of various oxygen species (O^{2-}, O_2^-, O_3^{2-}, $O_2^{\delta-}$ and O^-).[268] The radical ions O_2^-, O_2^{2-} and O_3^{2-} were also detected in the oxidative coupling of methane over $BaCO_3/LaOF$ and $Th - LaO_x/BaCO_3$ catalysts using the same method (see Ref. 269).[270] The radical ions O_2^- are formed in the presence of large amounts of carbonates. In this state, oxygen is an intermediate species in OCM. The O_2^-, O_2^{2-} and O_3^{2-} ions are stabilised in anionic vacancies. A reactive oxygen precursor induces abstraction of hydrogen from CH_4 to be converted into OH^- and O_2^-, or add an electron from the oxide lattice to yield the $O^{2-} + O^-$ couple.

The radical anions of O_2 were also detected in the study of OCM over LaOF and BaF/LaOF by IR spectroscopy *in situ*.[271] The O_2^- ions formed in the presence of oxygen react with CH_4 to give C_2H_6. It was thus concluded that the O_2^- radicals rather than O^- species that have not been detected played the role of active sites in the oxidative coupling of methane.

A detailed kinetic model of OCM involving heterogeneous and homogeneous reactions has been described.[272] The calculations were carried out for one of the most well-studied OCM catalysts, *viz.*, Li/MgO, at 650–700 °C, $CH_4 : O_2 = 2–12$, 200–1000 kPa and at the degree of CH_4 conversion of 10%–100%. This model comprised 10 catalytic and 39 gas-phase reactions. Some values of the constants for the elementary steps were taken from another study.[126] The model allowed a qualitative description of the pronounced increase in the degree of methane conversion with the increase in pressure from 200 to 1000 kPa. Under these conditions, the catalyst not only generated CH_3 radicals, but also acted as a radical trap. Presumably, the recovery of the active sites occurred through desorption of H_2O. Over Li/MgO the degree of conversion of the $CH_4 + O_2$ mixture at atmospheric pressure amounted to about 90%, while over Sn/Li/MgO it was only ~30%. According to this scheme, the conversion of methane into C_2 hydrocarbons is limited by heterogeneous-catalytic oxidation of CH_3 (see Ref. 273) rather than by gas-phase reactions. The reactions

$$O_2 + 2\,Li^+[\bullet] + 2\,Li^+O^{2-} \rightleftharpoons 4\,Li^+O^-,$$

$$Li^+O^- + CH_4 \longrightarrow Li^+OH^- + CH_3,$$

$$2\,Li^+OH^- \longrightarrow Li^+O^{2-} + Li^+[\bullet] + H_2O$$

occur on the surface of Li/MgO.
The symbol [•] designates the free-radical state.[272]

Valuable information for the elucidation of the mechanism of oxidative coupling of methane can be derived from the study[274] devoted to the formation of methyl radicals on the surface of O/Mo(110). Injection of oxygen onto the Mo(110) surface resulted in the formation of a two- or three-dimensional oxide layer. Subsequent injection of methane vapour resulted in the formation of CH_3O^- fragments, which retained stability at temperatures up to 200 °C over two-dimensional layers and withstood temperatures up to 430 °C over three-dimensional layers. At higher temperatures, the decomposition of CH_3O^- afforded H_2 and CH_3. This prompted a conclusion that methyl radicals are generated from CH_4 upon oxidative coupling of methane which proceeds *via* the methoxyl radical.

Using HREELS (High Resolution Electron Energy Loss Spectroscopy) and DSE (Diffraction of Slow Electrons), it was shown that it is the $Mo-CH_3$ layer rather than the $Mo-OCH_3$ layer that was formed as a result of injection of the methyl radicals onto the oxidised facet of Mo(100)–O (the degree of coverage was 0.8).[275] Decomposition of $Mo-CH_3$ yielded $Mo=CH_2$ and OH groups as could be evidenced from the results of spectral analysis.

A comparison of the results obtained in experiments where OCM was carried out in empty reactors and in reactors filled with CaO, La_2O_3/CaO or $SrO - La_2O_3/CaO$ led the authors to conclude[276] that the reason for the enhanced yields of the reaction products is the inhibition of the gas-phase oxidation due to quenching of free radicals that play the role of chain carriers in gas-phase reactions. At $T > 750$ °C, the intensity of inhibition and the yields of C_2 hydrocarbons decrease in the order: $SrO - La_2O_3/CaO > La_2O_3/CaO > CaO$, which parallels the order of basicities of the oxides. The role of the La_2O_3 component

of the catalyst consists of quenching CH_3 radicals or oxidation of CO, while that of CaO is dehydrogenation of C_2H_6 and that of SrO is inhibition of the gas-phase oxidation of CH_4.

A ten-step model of methane oxidation has been developed based on the analysis of numerous experimental data concerning OCM over various catalysts.[277] The interaction of Sn/Li/MgO with C_2H_4 and C_2H_6 is limited by abstraction of the hydrogen atom. The formation of HO_2 and its surface reactions should be taken into consideration in the heterogeneous–homogeneous process. The general scheme includes the following reactions:

$$O_2 + (S)^* \rightleftharpoons 2\,O^*,$$

$$CH_4 + O^* \longrightarrow CH_3 + OH^*,$$

$$C_2H_6 + O^* \longrightarrow C_2H_5 + OH^*,$$

$$2\,OH^* \longrightarrow H_2O + O^* + (S)^*,$$

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

$$2\,CH_3O^* + 5\,O^* \longrightarrow 2\,CO_2 + 3\,H_2O + (S)^*,$$

$$CO + O^* \longrightarrow CO_2 + (S)^*,$$

$$CO_2 + (S)^* \rightleftharpoons CO_2^*,$$

$$4\,HO_2 + (S) \longrightarrow 3\,O_2 + 2\,H_2O,$$

$$4\,CH_4 + O_2 + (S)^* \longrightarrow 4\,CH_3^* + 2\,H_2O,$$

$$4\,C_2H_6 + O_2 \longrightarrow 4\,C_2H_5 + 2\,H_2O,$$

$$4\,C_2H_4 + O_2 \longrightarrow 4\,C_2H_3 + 2\,H_2O,$$

$$2\,CO + O_2 \longrightarrow 2\,CO_2,$$

$$4\,CH_3 + 7\,O_2 \longrightarrow 4\,CO_2 + 6\,H_2O$$

(the active site on the surface of the catalyst is designated by the symbol *).[277]

The mechanism of the reaction $CH_4 + O_2 + CO_2$ over one of the best OCM catalysts, *viz*., $Na_2WO_4 - Mn/SiO_2$ was studied.[257] At 800 °C, the selectivity was 25% at 5% conversion. The role of CO_2 consisted of a decrease in the content of reactive oxygen responsible for deep oxidation. The following reaction mechanism was proposed:

$$CO_2 \longrightarrow CO + O^*,$$

$$O^* + CH_4 \longrightarrow CH_3 + OH^*,$$

$$2\,CH_3 \longrightarrow C_2H_6,$$

$$C_2H_6 + O^* \longrightarrow C_2H_4 + H_2O + (S)^*,$$

$$C_2H_6 \longrightarrow C_2H_4 + H_2.$$

c. Technological features

The attention of investigators is presently focused not so much over the search for novel OCM catalysts as over the technological design. The technological schemes of CH_4 conversion into $C_2H_4 + C_2H_6$ and aromatic products were described in a study by Lansford, one of the pioneers of OCM.[278] C_2 hydrocarbons were obtained over the active catalyst $Mn/Na_2WO_4/SiO_2$. The resulting mixture from the flow circuit entered first a quartz tube for dehydrogenation of C_2H_6 to C_2H_4 and then a reactor filled with Pd/Al_2O_3 for hydrogenation of admixtures of C_2H_2. After freezing-out CO_2 and H_2O, the mixture was fed onto a membrane impregnated with $AgNO_3$. The interaction of ethylene with silver yielded a π-complex able to penetrate through the membrane and decomposed in the second flow circuit with liberation of ethylene. When aromatic hydrocarbons were to be prepared from methane, the silver membrane in the flow circuit was replaced by a reactor with the Ga/HZSM-5 catalyst over which the conversion of C_2H_4 into benzene took place. Benzene was removed by cooling to −78 °C. The yields of C_2 hydrocarbons made up to 70%.

Combined two-step one-pot synthesis of C_2H_4 has been described. Its first step included exothermic oxidative coupling of methane over $La_{0.1}Ba_{0.9}O/CaO$ at 750 °C; the second step represented an endothermic reaction of ethane with CO_2 over MnO/SiO_2 at 800 °C:

$$C_2H_6 + CO_2 \longrightarrow C_2H_4 + CO + H_2O.$$

The yield of C_2H_4 in this combined two-step process was much higher than the yields from these two steps carried out in separate reactors. Continuous (130 h) operation analysis revealed stably high (27%) yield of ethylene.

When OCM was carried out over a 20% PbO–80% SnO_2 catalyst, which manifested sufficiently high stability, the yields of C_2 hydrocarbons did not exceed 8%.[255]

In some studies of OCM, oxygen-permeable membranes were used in order to increase the yields of C_2 hydrocarbons. Thus 1% SrO/La_2O_3 was used as a catalyst in a membrane reactor,[279] while Ag–Y–SrO was used for the preparation of oxygen-permeable membranes. Li/MgO was employed in an OCM reactor with an oxygen-permeable $BaCe_{0.8}Gd_{0.2}O_3$ membrane.[280] The yield of C_2 was 16.2%, *i.e*., higher than the yields from flow reactors under identical conditions. In yet another reactor with a 25% $Y_2O_3 - Bi_2O_3$ membrane, the yield of C_2 products reached 16% at up to 90% selectivity, *i.e*., exceeded those obtained in conventional flow reactors by 30%.[281] The experimental value of the activation energy of oxygen diffusion was 70 kJ mol^{-1}. In a study[282] where $La_{0.2}SrO_{0.4}Co_{0.8}Fe_{0.2}O_x$ was used as an active stable catalyst, methane and oxygen flows were fed onto the opposite sides of the Y–Zr–O membrane. Two different types of OCM membrane reactors were tested,[283] *viz*., disc-type membranes and cylindrical membranes based over $Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$. The oxygen flow was passed through the disk-type membrane at 900 °C at a rate of $1-3\times10^{-8}$ mol cm^{-2} s^{-1}. The maximum yields of C_2 products from tubular and disc-type membranes were 22% and 10.4%, respectively.

In yet another study,[284] OCM was carried out in the millisecond interval of the reaction times τ. Platinum and rhodium catalysts were supported over α-Al_2O_3 monoliths. The selectivity towards C_2 products was extremely low (0%–5%) where the reaction was carried out over $Rh/\alpha\text{-}Al_2O_3$ at $\tau \approx 1$ ms and somewhat higher over $Pt/\alpha\text{-}Al_2O_3$. The inlet temperature was below 200 °C, but it increased up to ~1500 °C at the outlet of the reactor, which favoured homogeneous reactions. At $\tau < 0.5$ ms, the selectivity towards C_2H_6 increased considerably (to 40%). With an increase in τ, the relative yields of C_2H_6 decreased, while the selectivity towards C_2H_4 passed through a maximum (~40%) at $\tau = 0.5$ ms. A further increase in τ to 1–2 ms caused a decrease in the selectivity towards C_2H_2 to 20%.

The progress achieved in the past two decades poses a question about practical implementation of the OCM technology. Joint investigations carried out by researchers of the Institute of Chemical Physics of the RAS and the Institute of Organic Synthesis (VNIIOS)[285] were aimed at elucidating the potentials of catalytic OCM reactions in gas chemistry. Based on the results obtained, it was concluded that production of ethylene from natural gas by OCM is technologically more efficient than of other products. Such a technology is especially attractive for Russia with its large reserves of inexpensive natural gas. Pilot-plant studies carried out in 120-ml reactors demonstrated the economic expediency of the development of OCM-based industrial technologies, especially in countries possessing cheap sources of natural gas (Russia and Iran). The production cost of ethylene obtained by this method can further be reduced owing to simultaneous production of water vapour and pure CO_2.

2. Oxidative dehydrogenation of ethane

Studies into oxidative dehydrogenation of ethane in reactors with millisecond residence times in the presence of Pt–Sn-catalysts supported over porous aluminium oxide monolith evoked substantial interest.[286, 287] Apparently, the role of a catalyst consisted of the promotion of oxidation of H_2 to H_2O without noticeable oxidation of ethane and ethylene and, as a consequence, without

any formation of significant amounts of CO and CO_2. The heat of oxidation of H_2 is sufficient for conducting endothermic dehydrogenation of C_2H_6 with high selectivity:

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O,$$

$$C_2H_6 \longrightarrow C_2H_4 + H_2,$$

$$C_2H_6 + \frac{1}{2}O_2 \longrightarrow C_2H_4 + H_2O.$$

On the whole, this process is exothermic, since hydrogen is formed in amounts exceeding those required for autothermal reactions and no additional fuel is needed. The catalyst effects the oxidation of hydrogen, while pyrolysis occurs in the gas phase, which is typical of homogeneous–heterogeneous reactions. Equally high selectivities at a similar degree of ethane conversion are attainable owing to very fast heating of ethane. Presumably, the high degree of conversion concomitant with short contact times can be attributed to enhanced release in the gas phase of reactive radicals generated by the catalyst surface.

These studies stimulated the development of a similar homogeneous process where ethane is injected directly into the diffusion flame of a hydrogen burner.[288] This made it possible to avoid the problems connected with the poisoning of the catalyst and to increase the process safety, since diffusion hydrogen flames are usually generated with conventional gas-jet burners in which hydrogen, ethane and oxygen are fed separately. The reaction temperature can be reduced to the level optimum for pyrolysis by feeding steam into the system. According to theoretical estimates, very high (>85%) selectivity towards ethylene at >70% conversion of ethane can be achieved. High efficiency of heat transfer is the main advantage of this process. Although an increase in temperature increases the rate of conversion (*i.e.*, reduces the reaction time), the selectivity towards ethylene decreases due to formation of acetylene. Moreover, at the degree of ethane conversion higher than 60%, the selectivity of the reaction drops drastically due to simultaneous competing coupling reactions yielding heavier molecules. However, this problem can be circumvented by the addition of steam.

3. Oxidative methylation

Relatively few papers devoted to oxidative methylation first discovered by Khcheyan[289] about 25 years ago have recently been published. Oxidative methylation of acetonitrile into acrylonitrile has been studied.[290] The well-known Lansford catalyst (Li/MgO) containing 25% of lithium was found to be the most efficient by virtue of its ability to produce the maximum number of active sites $[Li^+O^-]$. Other known catalysts of oxidative coupling of methane (Sm_2O_3, La_2O_3, CaO and Bi_2O_3) did not manifest any activity in the oxidative methylation and only deep oxidation took place. The basicity of the catalyst surface was not important in this case. At 750 °C, the degree of conversion reached 50% with 35% selectivity.

Zeolites impregnated with CsCl manifested high activity in the oxidative methylation of toluene.[291] The activities of zeolites did not depend on their structures. The activities of Cs-substituted catalysts of oxidative methylation of toluene increased in the following order: CsX < CsY < Cs–ZSM-5 < $CsAlPO_4$-5.[291] The most active catalyst, *viz.*, $CsAlPO_4$-5, afforded $C_6H_5C_2H_5 + C_6H_5CH{=}CH_2$ in 16% yield with 75% selectivity at 750 °C. Halides supported over zeolite KY were also tested as catalysts; their activities decreased in the following order: NaBr/KY > KBr/KY > NaCl/KY.

4. The Andrussov reaction

Oxidative ammonolysis of methane resulting in HCN was discovered in the 1930's by Andrussov who was working in Germany at that time. The reaction

$$CH_4 + NH_3 + 1.5\,O_2 \longrightarrow HCN + 3\,H_2O$$

was carried out in the autothemic regime (~1000 °C) over Pt gauzes in the millisecond range of residence times. It was assumed[292] that this process includes the following reactions:

$$CH_4 + O_2 \longrightarrow HCO_2H + H_2,$$

$$HCO_2H + NH_3 \longrightarrow HCN + 2\,H_2O,$$

$$HCN + H_2O \longrightarrow NH_3 + CO.$$

The thermodynamic equilibrium yield of HCN (8.5%) was obtained at a contact time of 4×10^{-5} s. The parameters could be improved by increasing the rate of supply of the starting mixture to 9000–10 000 $m^3\ h^{-1}$, forced reduction of the reaction temperature from 980 to 850 °C and cooling of the exit gas to 300 °C within no more than 0.01 s. A special reactor for non-equilibrium processes has been designed.[293] The addition of small amounts of hydrogen to the $CH_4 + NH_3 + O_2$ mixture that reacted on a Pt–Rh gauze increased the selectivity towards HCN from 74% to 82%, whereas after addition of air the increase in the selectivity was even greater (86%), but the conversion of NH_3 was lower.

5. Cold-flame and nonlinear phenomena associated with oxidation of lower alkanes

Studies of nonlinear phenomena associated with oxidation of lower alkanes, such as the generation of cold flames and region of negative temperature coefficient (NTC), are currently underway. Simulation of NTC in the low-temperature oxidation of propane and butane has been described.[294] An extended mechanism of low-temperature oxidation of hydrocarbons from C_1 to C_4, which is based on the well-known GRI-Mech mechanism (see Ref. 295), has been proposed. Propyl peroxide radicals and their isomers are the main species that induce the appearance of NTC in the oxidation of propane. Based on the results of simulation, it became possible to obtain a virtually quantitative (with the accuracy of 10 K) agreement with the experimentally determined values of minimum and maximum temperatures in NTC and very good coincidence of the shapes of the temperature dependences of the induction period. The rationale for this phenomenon[295] is consistent with the widely accepted notion of an increased contribution of abstraction of the nonreactive radical HO_2 from the propyl peroxide radical at elevated temperatures:

$$C_3H_7OO \longrightarrow C_3H_6 + HO_2,$$

which is equivalent to the decay of the radicals under the given conditions. This results in a decrease in the rate of the overall branching-chain reaction. With further increase in temperature, the hydrogen peroxide formed by recombination of HO_2 radicals becomes itself a source of OH radicals, which is equivalent to elimination of this channel of the chain termination.

* * *

The analysis of the published data suggests that in-depth studies of oxidative conversion of methane are underway, especially in those areas where their industrial potential is especially high. The level of activities in the field of catalytic oxidation of methane to synthesis gas is steadily expanding against the decreasing number of publications devoted to oxidative coupling of methane or its oxidation to oxygenates. The most recent trend is towards deletion the distinctions between heterogeneous catalysis and homogeneous processes, which are being more often considered as an integral homogeneous–heterogeneous process, and increasing the role of kinetic simulations and modern physical methods of analysis *in situ*.

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