Translated from *Uspekhi Khimii* **58** 38–57 (1989) U.D.C. 542.954

The mechanism of the partial oxidation of methane

M Yu Sinev, V N Korshak, O V Krylov
Institute of Chemical Physics, USSR Academy of Sciences, Moscow

ABSTRACT. The principal characteristics of the homogeneous and heterogeneous-catalytic conversion of methane into condensation products (C_2 and C_3 hydrocarbons) and partial oxidation products (methanol and formaldehyde) are considered. Data are presented concerning the most effective catalysts and data relating to the mechanism of the activation of methane on oxide and oxide halide catalysts, the nature of the active centres, and the kinetics of the partial oxidation of methane are analysed. It is shown that the oxidative condensation of methane in the presence of the catalysts considered is a heterogeneous-homogeneous process, which imposes special requirements in its practical realisation.
The bibliography includes 118 references.

Contents

I. Introduction 22
II. Reactions of methane in the gas phase 22
III. Heterogeneous-catalytic oxidation of methane 24

I. Introduction

The limited resources of petroleum and the constant increase in the cost of its extraction have brought to the fore the problem of the search for an alternative raw material for the chemical and petrochemical industry.

In the immediate future natural gas, and primarily its principal component (methane), may become such raw material.[1] Methane is also a side product in a whole series of reactions involved in the processing of organic raw material, including coal, which are likely to become the principal source of organic intermediate products and motor fuels.[2] This gives rise to the problem of devising effective processes for the conversion of methane into valuable products—methanol, formaldehyde, lower alkanes, etc.

Together with its practical importance, the problem of the processing of methane is of considerable theoretical interest, since it is associated with research into the possibility of activating an extremely stable molecule, whose reactivity is significantly lower than that of the target products.

Studies on the heterogeneous catalytic oxidation of methane to useful products can be arbitrarily divided into two parts. One of these is associated with the synthesis of valuable oxygen-containing compounds—methanol and formaldehyde. This aspect has been developing for a very long time and definite results concerning the understanding of the process mechanism and of the influence of the nature of the active centres of the catalysts on their activity and selectivity have been obtained. However, the yields of the useful products on stably operating catalysts do not exceed 3% for methanol and 5–8% for formaldehyde in the oxidation of methane by oxygen or air without the addition of various compounds (nitrogen oxides, halogeno-derivatives) as oxidants and initiators. Thus a significant increase in the yields of valuable oxygen-containing compounds has not so far been achieved in the heterogeneous-catalytic oxidation of methane compared with the homogeneous oxidation.

The second aspect—the catalytic oxidtive condensation of methane to higher hydrocarbons (mainly to ethane, ethylene, propene, and acetylene)—began to develop comparatively recently, about five years ago. Nevertheless, during this extremely brief period a considerable number of effective catalysts have been developed, which makes it possible, for example, to achieve a yield of C_2 hydrocarbons up to 30% relative to the methane passed through the system.

Definite progress has been made also in the understanding of the mechanism of the oxidative condensation of methane; multistage schemes and the simplest kinetic models have been proposed, permitting an explanation of the characteristics of the process including homogeneous stages in which the radicals $CH_3^{\cdot}$ and $CH_3O_2^{\cdot}$ participate.

We must emphasise that the oxidation of methane on the majority of catalysts apparently includes a stage involving the heterogeneous generation of $CH_3^{\cdot}$ radicals and stages in which they undergo further reactions both in the gas phase and on the surface. It therefore appears useful to carry out a brief survey of investigations into the gas-phase oxidation of methane, before proceeding to the consideration of studies on its heterogeneous-catalytic oxidation. Among the latter, most attention will be devoted to studies on oxidative condensation—in our view, the most promising aspect of the selective catalytic oxidation of methane.

II. Reactions of methane in the gas phase

Homogeneous reactions of methane in the gas phase have been studied in greatest detail at the present time; investigations on these lines have been prosecuted for many decades and their results have been surveyed in a number of reviews (see, for example, Refs. 3–5) and new data go on being added.

Owing to the high thermodynamic stability of methane, its conversion into, for example, hydrocarbons at a relatively low temperature is impossible because of the virtually complete shift of

the equilibrium towards methane.[6] With increase in temperature, the equilibrium is displaced and the possibility of the formation of appreciable amounts of hydrocarbons appears. It has been established[3] that the pyrolysis of methane takes place at temperatures above 700 °C in accordance with the scheme

$$CH_4 \xrightarrow{a} C_2H_6 \xrightarrow{b} C_2H_4 \xrightarrow{c} C_2H_2 \xrightarrow{d} \text{aromatic hydrocarbons, coke.} \quad (1)$$

The primary radical formed in the system is $CH_3^{\cdot}$:

$$CH_4 \rightarrow CH_3^{\cdot} + H^{\cdot}. \quad (2)$$

The activation energy for reaction (2) is 90–107 kcal mol^{-1}. Admixtures of other hydrocarbons as well as halogens and oxygen have an initiating effect.

The initiation stage (2) is followed by the chain propagation and termination stages, which can be represented in the following simplified form:

$$H^{\cdot} + CH_4 \rightarrow CH_3^{\cdot} + H_2, \quad (3)$$

$$2CH_3^{\cdot} \rightarrow C_2H_6, \quad (4)$$

$$CH_3^{\cdot} + H^{\cdot} \rightarrow CH_4. \quad (5)$$

The activation energies for the overall stages *b*, *c*, and *d* in Scheme (1) are respectively 64–90, 35–65, and 22–50 kcal mol^{-1}, which indicates a higher reactivity of the condensation products compared with the initial methane.

According to Roscoe and Thompson,[7] the C_2 and C_3 hydrocarbons are formed via a series of radical stages:

$$\begin{gathered} CH_3^{\cdot} + C_2H_6 \rightarrow C_2H_5^{\cdot} + CH_4;\ CH_3^{\cdot} + C_2H_4 \rightleftarrows n\text{-}C_3H_7^{\cdot}; \\ C_2H_5^{\cdot} \rightarrow C_2H_4 + H^{\cdot};\ n\text{-}C_3H_7^{\cdot} \rightarrow C_4H_8 + H^{\cdot}; \\ CH_3^{\cdot} + C_2H_4 \rightarrow C_2H_3^{\cdot} + CH_4;\ CH_3^{\cdot} + C_3H_5^{\cdot} \rightleftarrows C_3H_5^{\cdot} + CH_4; \\ C_2H_3^{\cdot} \rightarrow C_2H_2 + H^{\cdot};\ C_3H_5^{\cdot} \rightarrow CH_2{=}C{=}CH_2 + H^{\cdot}, \text{ etc.} \end{gathered} \quad (6)$$

It was shown in the same study by numerical calculation that the concentration of $CH_3^{\cdot}$ radicals exceeds by more than an order of magnitude the overall concentration of all other radicals. The calculated formation curves for the molecular products at 765 °C describe satisfactorily the experimental data:[8,9] for reaction times up to 500 s, the concentration of ethane is highest among all the hydrocarbon products, while for longer times that of ethylene is highest; if the reaction time exceeds 2290 s, the concentration of propene is higher than that of ethane and, whatever the reaction time, the concentration of propene is 3–4 times higher than that of acetylene. Alkanes heavier than ethane (propane, butane, etc.) are not formed.

The rate of conversion of methane increases significantly in the presence of a large surface area, apparently as a result of the acceleration of the initiation stage. On a carbon surface, and any surface becomes coated with carbon on pyrolysis with deposition of coke,[3] the effective activation energy for the initiation stage may fall to ~50 kcal mol^{-1}.[10] A change in the composition of the surface during the process can influence its rate and direction. Thus, in the presence of MgO [11] at 900 °C, the degree of conversion of methane falls from 22 to 8% during the first 6–7 h, after which it retains a stationary value; however, the yield of hydrocarbons increases from 0.8 to 2.4%. Whereas in an empty quartz reactor the formation of hydrocarbons is not observed for a contact time less than 3 s, with increase in contact time to 10 s the yields of hydrocarbons on the coke-saturated MgO and in the empty quartz reactor are similar.

It must be emphasised yet again that the attainment of high yields of hydrocarbon methane condensation products is limited by the unfavourable equilibrium position even at relatively high temperatures (700–900 °C). Thermodynamic prohibition of the conversion of methane is removed in oxidation processes which take place with a decrease in free energy.

The characteristic features of the homogeneous oxidation of methane have been studied most fully compared with other hydrocarbons.[12] This process is complex, proceeds via a branched chain mechanism, and includes several tens of stages. A whole series of kinetic models have now been proposed for the description of the homogeneous oxidation of methane (see for example, Refs. 13–17). Each of them corresponds to definite homogeneous oxidation reaction conditions (temperature and pressure range, concentration of the components of the reaction mixture, macrokinetic characteristics of the system).

In all the mechanisms proposed, it is assumed that chain initiation takes place in the following stage characterised by an activation energy of ~50 kcal mol^{-1}:[18]

$$CH_4 + O_2 \rightarrow CH_3^{\cdot} + HO_2^{\cdot}. \quad (7)$$

Chain propagation takes place in the following stages:

$$\begin{gathered} CH_3^{\cdot} + O_2 \rightleftarrows CH_3O_2^{\cdot};\qquad CH_3O^{\cdot} \rightarrow CH_2O + H^{\cdot}; \\ CH_3O_2^{\cdot} + CH_4 \rightarrow CH_3OOH + CH_3^{\cdot};\qquad H^{\cdot} + CH_4 \rightarrow H_2 + CH_3^{\cdot}; \\ CH_3O_2^{\cdot} + CH_3^{\cdot} \rightarrow 2CH_3O^{\cdot};\qquad CHO_2^{\cdot} + CH_2O \rightarrow CH_3OH + CHO^{\cdot}; \\ CH_3O_2^{\cdot} + CH_4 \rightarrow CH_3OH + CH_3O^{\cdot};\qquad CH_3O^{\cdot} + O_2 \rightarrow CH_2O + HO_2^{\cdot}; \\ HO_2^{\cdot} + CH_4 \rightarrow H_2O_2 + CH_3^{\cdot};\qquad CHO^{\cdot} + O_2 \rightarrow CO + HO_2^{\cdot}; \\ CH_3O_2^{\cdot} \rightarrow CH_2O + OH^{\cdot};\qquad CO + HO_2^{\cdot} \rightarrow CO_2 + OH^{\cdot}; \\ OH^{\cdot} + CH_4 \rightarrow CH_3^{\cdot} + H_2O;\qquad 2CH_3O_2^{\cdot} \rightarrow CH_3OH + CH_2O + O_2; \\ CH_2O + HO_2^{\cdot} \rightarrow CHO^{\cdot} + H_2O_2;\qquad 2CH_3O_2^{\cdot} \rightarrow 2CH_3O^{\cdot} + O_2, \text{ etc.} \end{gathered} \quad (8)$$

Chain branching occurs in the stages

$$H_2O_2 + M \rightarrow 2OH^{\cdot}, \quad (9)$$

$$CH_2O + O_2 \rightarrow HO_2^{\cdot} + CHO^{\cdot}, \quad (10)$$

$$CH_3OOH \rightarrow CH_3O^{\cdot} + OH^{\cdot}. \quad (11)$$

Chain termination can occur in stages (4) and (5) and also as a result of the destruction of active species ($HO_2^{\cdot}$, $CH_3O_2^{\cdot}$, $CH_3^{\cdot}$, OH, H_2O_2, CH_3OOH) on the reactor walls. The kinetic parameters of the radical destruction processes on the walls are frequently unknown and are estimated from the correspondence of the results of the numerical computation to the experimental data (see, for example, Vardanyan et al.[14]). The rate constants for the majority of the homogeneous stages found by different methods are available in the literature.[19–22]

The data accumulated for the homogeneous gas-phase methane oxidation processes show that the partial oxidation products formed (CH_2O, CH_3OH) exhibit a higher reactivity under the process conditions compared to methane and undergo further successive transformations into extensive oxidation products. As a result, the yield of formaldehyde at 500–600 °C cannot exceed 0.5% relative to the methane passed through the system.[13] The preparation of

methanol requires an increase in pressure to tens of atmospheres;[5,17,23] the yield of CH_3OH can then reach several per cent relative to the methane passed through the system at 400–600 °C.

III. Heterogeneous-catalytic oxidation of methane

The most realistic method of increasing the yield of target products may involve the oxidation of methane in the presence of heterogeneous catalysts. However, for a long time the attempts to create effective catalysts for the conversion of methane into valuable products on the basis of traditional catalytic systems were unsuccessful; in the presence of transition metals and their oxides (see, for example, Refs. 24–26), extensive oxidation of methane mainly takes place; the efficiency of zeolitic catalysts in relation to the partial oxidation in the presence of oxygen is also low.[27]

However, in recent years definite progress has been achieved in the search for catalysts and conditions for the process leading to the partial oxidation of methane.

1. Partial oxidation of methane to oxygen-containing compounds

It was noted above that at elevated pressures it is possible to drive the gas-phase methane oxidation process towards CH_3OH. The application of catalysts based on zinc, cadmium, and nickel oxides, which are solid solutions,[28] and the use of a high pressure (up to 100 atm)[29] make it possible to achieve a yield of CH_3OH up to 2% relative to the methane passed through the system for a selectivity of about 80%. Like other heterogeneous catalysts,[5] this system does not give rise to a significant increase in the yield of methanol compared with homogeneous oxidation.

A wide range of oxide and phosphate catalytic systems have been investigated in the reaction involving the oxidation of methane to formaldehyde.[30,31] Catalysts which are weakly reduced by hydrogen (SiO_2, BPO_4, $AlPO_4$) exhibit a high selectivity with respect to CH_2O. Highly passive catalysts are most active as regards CH_2O, which is attributed to the easier desorption of the products from their surfaces. In the series investigated, tin phosphate is the optimum catalyst[32] on which the yield of CH_2O can reach 16% under conditions with circulation of the reaction mixture and the freezing out of the product during the cycle. In the flow regime, the yield of CH_2O during one pass does not exceed 2%.[33]

When aluminosilicates (with an Al_2O_3 content of 10–11%), modified by the addition of metal (Fe, Zr, V, Ni, Mo, Cu, Cd, Bi, Cr) oxides,[34] are used as catalysts, it is also possible to increase the yield of CH_2O (1.9% relative to the methane passed through the system on aluminosilicate containing 1.5% of Fe_2O_3). The maximum yield of CH_2O (2.6%) was obtained on aluminosilicate with added 2% of cerium phosphate and 0.05–0.06% of P_2O_5 at 750 °C. In the presence of this catalyst, it is possible to reduce the reaction temperature approximately by 100 °C with simultaneous increase in the CH_2O yield to 5–5.5% as the result of the introduction of 0.2–0.5% of $(CH_3)_2O$ into the contact zone.[35]

The addition of halogen-containing compounds into the reactant stream also entails an increase in the yield of CH_2O. Catalysts containing deposited transition metal (Ce, Mo, V, Fe, Co) oxides have been described.[36] At 450–600 °C and after the addition of up to 1 mole of HCl per mole of CH_4 to the initial mixture, they make it possible to obtain a yield of CH_2O up to 15% relative to the methane passed through the system.

When a deposited palladium catalyst (0.5% of the oxide on Al_2O_3) is used,[37] the introduction of 5 mole % (relative to methane) of CH_2Cl_2 into the stream of the 5 : 1 mixture of air and methane lowers the degree of conversion of methane at 475 °C from 20 to 13% with a simultaneous increase in the CH_2O yield from 0 to 6%. Experiments involving the introduction of CH_2Cl_2 into the mixture of CH_2O with air showed that this entails the suppression of the subsequent oxidation of formaldehyde.

Detailed investigation of the partial oxidation of methane to CH_2O [38] by methods involving separate calorimetric measurements and EPR with the freezing out of radicals showed that, in the presence of KSK silica gel and γ-Al_2O_3, the process takes place partly in the bulk of the gas phase. Evidence was obtained for a heterogeneous-homogeneous mechanism of the oxidation of methane, according to which the gas-phase processes lower the selectivity with respect to CH_2O. The low process selectivity on Al_2O_3 can be explained by the high rate of successive conversion of formaldehyde into carbon oxides as a result of the additional oxidation and decomposition into CO and H_2. The influence of the modification of silica gel by the addition of ZnO, SrO, CdO, B_2O_3, Al_2O_3, CeO_2, Bi_2O_3, V_2O_5, MoO_3, and WO_3 on the yield of methane oxidation products has been investigated. The maximum yield of CH_2O (up to 3.6%) has been obtained on a specimen modified with ZnO.

A communication[39] describing the formation of a complex catalyst containing Fe, Mo, Ni, Mg, and Bi oxides on SiO_2, which makes it possible to obtain CH_2O at 650 °C by oxidising methane with a selectivity of 86.5% for a conversion of 8.9%, has been published recently.

A significant increase in the yield of oxygen-containing products of the partial oxidation of methane can be achieved using N_2O as the oxidising agent. The replacement of O_2 by N_2O leads to an increase in the degree of conversion of methane on the 2% MoO_3/SiO_2 catalyst[40,41] at 550 °C from 0.5 to 6%; the selectivities with respect to CH_3OH and CH_2O are then 38 and 55% respectively. The maximum yield of the partial methane oxidation products is observed when water is added to the initial mixture: at p_{H_2O} = 0.18 to 0.20 atm, the degree of conversion of methane is 26% for selectivities with respect to CH_3OH and CH_2O of 80 and 19% respectively, in the absence of water, the degree of conversion is approximately 4% for an overall selectivity of about 60%. Under the conditions of thermoprogrammed desorption, C_2H_6 and C_2H_4 are evolved at relatively low temperatures (100–200 °C) after the successive admission at 25 °C of N_2O and CH_4 to a specimen, containing molybdenum (V) ions,[41] which had been reduced beforehand; the maximum evolution of CH_3OH occurs at a temperature above 450 °C. Traces of C_2 hydrocarbons are present in the reaction mixture also under the conditions of the continuous supply of a mixture of CH_4 and N_2O.[40,41]

The proposed process mechanism includes the following stages leading to the formation of CH_3OH and CH_2O:[43]

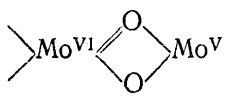
$$
\begin{aligned}
&Mo^{V} + N_2O \rightarrow Mo^{VI}O^{-} + N_2,\\
&Mo^{VI}O^{-} + CH_4 \rightarrow Mo^{VI}OH^{-} + CH_3^{\cdot},\\
&Mo^{VI}O^{2-} + CH_3^{\cdot} \rightarrow Mo^{V}OCH_3,\\
&Mo^{V}OCH_3^{-} + H_2O \rightarrow Mo^{V}OH^{-} + CH_3OH,\\
&Mo^{V}OH^{-} + Mo^{VI}OH \rightarrow Mo^{V} + Mo^{VI}O^{2-} + H_2O,\\
&Mo^{V}OCH_3^{-} + Mo^{VI}O^{2-} \rightarrow Mo^{VI} + Mo^{V}OH + CH_2O.
\end{aligned}
\qquad (12)
$$

The processes

$$8Mo^{VI} + 4O^{2-} + CH_4 \rightarrow 8Mo^{V} + 2H_2O + CO_2, \quad (13)$$

$$2Mo^{V} + N_2O \rightarrow 2Mo^{VI} + N_2 + O^{2-}, \quad (14)$$

can lead to non-selective oxidation. It has been suggested that the active centre has the structure



A difference in the behaviour of the surface CH_3O^- groups on deposited MoO_3, where they react in accordance with Scheme (12) as presented above, and on MgO where their only reaction pathway is decomposition into CO and H_2 [44] has been noted.[42] Nor can one exclude also the possibility of the formation of CH_3OH via the interaction of the $CH_3^{\cdot}$ radicals with water or Si—OH groups.[43]

It has been shown[45] that the mechanisms of the formation of CH_2O at temperatures below and above 540 °C on the 2% MoO_3/SiO_2 catalyst are different. There is a possibility of both the direct formation of CH_2O from the CH_3O^- groups and of the successive conversion of methanol into formaldehyde; the effective activation energies E_a for these two processes are respectively 82 ± 4 and 41 ± 4 kcal mol^{-1} (the latter value virtually agrees with E_a for the formation of CH_3OH, which is 40 ± 2 kcal mol^{-1}).

The 2% V_2O_5/SiO_2 catalyst, in which the deposited component is present as a submonolayer of isolated vanadium ions,[46] also exhibits activity in the formation of partial oxidation products of methane in the presence of N_2O.[47] This system operates at a lower temperture compared with MoO_3/SiO_2; the activation energies E_a for the formation of CH_3OH and CH_2O are respectively 40 ± 4 and 22 ± 2 kcal mol^{-1}. A difference between the mechanisms of the formation of CH_2O on the above systems has been noted: in the case of V_2O_5/SiO_2 there is no successive conversion of CH_3OH into CH_2O and formaldehyde is formed only in the course of the dehydrogenation of the surface CH_3O^- group occurring simultaneously.

The possibility of the conversion of the CH_3O^- group on $Bi_2O_3-SnO_2$ catalysts into both CH_2O (in the absence of water) and CH_3OH (in the presence of water), on the one hand, and into C_2H_6, on the other, has been postulated.[48] In the presence of N_2O at 550 °C, the selectivity with respect to CH_2O on these catalysts can reach 92.2% for a degree of conversion of methane of 2.6%. In the absence of N_2O, methane can be oxidised by the oxygen of the catalyst to CH_2O with a selectivity of about 80%, the activity falling gradually.

The increase in the yield of the methane partial oxidation products in the presence of N_2O as the oxidant has been attributed to the oxidation on the catalyst surfaces of the radical-ions $O^{\cdot-}$, which are capable of abstracting a hydrogen atom from the methane molecules.[49]

It is notable that the mode of the methane oxidation process can change when O_2 is replaced by N_2O. Thus mainly carbon oxides are formed on zeolitic catalysts when O_2 is used;[27] the replacement of O_2 by N_2O leads to the formation of aromatic hydrocarbons, the overall yield at 400 °C on a decationated zeolite with the ratio $Al_2O_3:SiO_2 = 1:68$ can reach 10% for a conversion of methane of 25%.[50] With decrease in the degree of cationation, the yield of hydrocarbons falls.[51]

As already mentioned, when O_2 is used as the oxidant, it is not possible to achieve an appreciable yield of the products of the partial oxidation of methane on oxide and zeolitic catalysts. However, recently major progress has been achieved in effecting another process—the oxidative condensation of methane with formation of C_2 and higher hydrocarbons.

2. Oxidative condensation of methane

(a) Alternate oxidation–reduction of oxide systems

The possibility of obtaining an appreciable yield of the products of the oxidative condensation of methane was apparently first demonstrated in a patent.[52] The process is carried out with methane supplied to solid catalysts containing 0.01–0.2% of a Group VIII or IB metal, chromium and molybdenum oxides, or tungsten, barium, lanthanum, and other oxides on the MgO, TiO_2, ZrO_2, and Al_2O_3 carriers. In particular, when methane is supplied at a temperature of about 700 °C to a specimen obtained by the successive treatment of γ-Al_2O_3 with solutions of magnesium, barium, and chromium nitrates, with an intermediate heat treatment, and then with a solution of H_2PtCl_6, it is possible to obtain 8% of C_2H_4, 3.2% of C_2H_6, 0.056% of C_4H_8, and 14.4% of benzene. Furthermore, 19.3% of methane is converted into condensation products, from which C_2H_4 and C_6H_6 are formed on treatment with water vapour or O_2. The proposed process mechanism involves the formation of dehydrogenated forms on the surface as far as coke and their subsequent interaction with CH_4 to form higher hydrocarbons.

Keller and Bhasin[53] investigated the formation of ethane and ethylene on alternate exposure of metal oxides deposited on α-Al_2O_3 to methane and air. The Mn, Cd, Sb, Tl, Pb, and Mg oxides proved to be the most active and selective at 800 °C. The overall yield of C_2 hydrocarbons on the best specimen, containing manganese, was 5% relative to the methane passed through the system for an 11% conversion. A mechanism was proposed for the formation of the oxidative condensation products:

$$\begin{gathered} CH_4 + M^{(2n)+}O_n^{2-} \rightarrow M^{(2n-2)+}O_{n-1}^{2-} + OH_{ads} + CH_{3,ads}, \\ 2CH_{3,ads} \rightarrow CH_3CH_{3,ads}, \\ 2OH_{ads} \rightarrow H_2O + O_{ads}, \\ 2M^{(2n-2)+}O_{n-1}^{2-} + O_2 \rightarrow 2M^{(2n)+}O_n^{2-}. \end{gathered} \quad (15)$$

Analogous processes leading to the formation of the products of the oxidative condensation of methane with separate supply of methane and oxygen to a solid catalyst have been described in the patent literature.[54–61] The active phase of the catalyst employed contains Mn, Sb, In, Ge, Pb, Sn, and Bi oxides with added alkali or alkaline earth metal cations and phosphate ions on carriers. The selectivity with respect to the sum of hydrocarbons in the first oxidation-reduction cycles can exceed 80% for a methane conversion of about 15%.[55] The Mn/γ-Al_2O_3 catalyst is characterised by a much lower selectivity than Mn/SiO_2.[62] In the latter case, 0.4 ± 0.05 of a gram-atom of oxygen per gram-atom of Mn can be removed reversibly from the catalyst. The increase in the selectivity and stability of the 15% Mn/SiO_2 catalyst when it is modified by the addition of 5% of $Na_4P_2O_7$ [63] has been explained by the decrease in acidity and a change in the phase composition. The introduction of halogen-containing compounds (for example, CH_3Cl) into the stream of methane makes it possible to increase the selectivity to 85–93% for conversions up to 29%.[60]

Although an appreciable yield of the products of the oxidative condensation of methane can be achieved in the processes described, they suffer from two significant disadvantages: the difficulty of achieving in practice an alternating supply of the reactants and a gradual (in many cases extremely rapid) loss of activity by the solid catalyst.

(b) The performance of the process in the continuous regime

After the communications in which the oxidative condensation of methane involving the use of the lattice oxygen of oxide systems was described, data were published on catalysts which made it possible to carry out the process in the continuous regime. For this purpose, use is made of systems which had been employed earlier as sources of lattice oxygen (Mn, Sn, In, Ge, Pb, Sb, Bi, Pr, Tl, Cd oxides on carriers promoted by alkali or alkaline earth metals and stabilised by phosphate ions).[64-67] For example, when a CH_4:air = 1:1 mixture is supplied to a catalyst containing 10% each of Mn (in the form of oxides) and $Na_4P_2O_7$ on SiO_2, the degree of conversion of methane can reach 24.1% for an overall selectivity with respect to C_2 hydrocarbons of 57%.[64]

If N_2O is used as the oxidant, then, for a methane conversion of 28.4%, the selectivity with respect to the sum of C_2 and higher hydrocarbons can reach 68% (800 °C, catalyst—12.5% $NaMnO_4$ on MgO).[65]

In the case of deposited catalysts containing PbO, the highest yield of hydrocarbons is obtained when Al_2O_3 is used as the carrier.[68] At 740 °C, CH_4 and O_2 pressures in the initial mixture of 0.7 and 0.07 atm respectively, and the virtually complete conversion of O_2, the selectivity of the PbO/Al_2O_3 catalysts increases with increase in the PbO content, reaching a maximum value of 57.7% (with respect to the sum of C_2 and C_3 hydrocarbons) for a PbO concentration of 36%. The introduction of 2% of Na_2O into the 6.5% PbO/Al_2O_3 catalyst increases the selectivity with respect to hydrocarbons from 12.9 to 35.4%. The selectivity of catalysts on different carriers decreases in the sequence SiO_2 > Al_2O_3 > aluminosilicates, but the activity of the systems based on SiO_2 is extremely low.

Catalysts obtained by depositing PbO on carriers with a high alkalinity (MgO, CaO, β-Al_2O_3) are even more effective.[69] The conversion of methane and the selectivity with respect to C_2 hydrocarbons on the 5% PbO/MgO catalyst at 750 °C are respectively 13 and 72%.[70] The influence of the basicity of the carrier on the efficiency of the oxidative condensation has been emphasised.[69,70]

After prolonged use of the PbO/Al_2O_3 catalysts at 800 °C (30 h), the selectivity falls from 40 to 7%,[71] which has been attributed to the possible entrainment of lead by the gas stream.

In the series of catalysts containing Ga, In, and Tl oxides on an aluminosilicate carrier (19 mole % SiO_2), the highest yield of C_2 hydrocarbon (2.3%) was observed for the thallium catalysts.[72] Catalysts on aluminomagnesium carriers (20-50 mole % MgO) have a higher activity.

Oxidation catalysts of a new type, not containing metal ions in a variable oxidation state, based on alkaline earth metal oxides modified by alkali metal cations with similar (or smaller) ionic radii were first described and investigated in detail by Lunsford and co-workers.[73-78] These catalysts possess a high activity and selectivity in the oxidative condensation of methane, which has been attributed to the possibility of the formation of substitutional defects in the cationic sublattice and to the appearance of centres of the type Li^+O^-, which can participate in the activation of methane molecules. Thus, on the 7% Li/MgO catalysts, obtained by impregnating MgO with a solution of Li_2O_3 and subsequent heat treatment at 720 °C, the yield of C_2 hydrocarbons, from an initial mixture in which the CH_4 and O_2 pressures were 58 and 36 mm Hg, reached 19.4% (the yield relative to MgO was 1%) and diminished with increase in the reactant concentrations in the initial mixture while their ratio remained constant.[73] With increase in the relative amount of CH_4, the selectivity increases and the degree of conversion falls. CH_3OH and CH_2O are formed in trace amounts. The 15% Na/CaO catalyst also exhibits a high efficiency (the selectivity with respect to hydrocarbons is 52% for a methane conversion of 22%). On the other hand, if the ionic radius of the alkali metal cation is greater than that of the alkaline earth metal cation, the catalytic properties of the system are much worse: on the 20% Na/MgO catalyst, the degree of conversion of methane is 12% and the selectivity with respect to hydrocarbons is 18%.[77]

However, it has been shown, that in the series of catalysts obtained by impregnating MgO with metal (alkali, alkaline earth, transition, etc.) nitrate solutions, specimens containing more than 10% of Na_2O are the most effective: the yield of C_2 hydrocarbons reaches 19.5-22.4% relative to the methane passed through the system at 750-800 °C for a methane concentration in the initial mixture of about 3% (CH_4:O_2 = 2:1).[79] When this method is used to introduce the additive, the lithium-containing catalysts are less effective (the yield of C_2 hydrocarbons at 750 °C is about 9%). The high efficiency of the sodium-containing catalysts has been explained by the influence of Na^+ on the MgO structure.

The study of a large number of metal oxides[80] has led to the conclusion that the highest selectivity is manifested by lanthanide metal oxides (with the exception of Ce, Pr, and Tb). Among them, the most effective is Sm_2O_3, in the presence of which the selectivity with respect to C_2H_6 at low O_2 concentrations (1.6%) can reach 100% at 700 °C.[81]

The modification of Sm_2O_3 by alkali metal ions, carried out by impregnating the catalyst with solutions of their carbonates and subsequent heat treatment, increases the yield of C_2 hydrocarbons.[82] The specimen containing 10 mole % of Li_2O, on which the yield of C_2 hydrocarbons reaches 21% compared with 12% for the unmodified Sm_2O_3 is optimal (750 °C, CH_4 and O_2 pressures in the initial mixture 50 and 20 mmHg respectively).

The modification of Sm_2O_3 with 20 mole % of LiCl instead of Li_2CO_3 [82] increases the yield of C_2H_4 by a factor of 1.5 (to 16.8%) with a slight decrease of the overall yield of the C_2 hydrocarbons. However, such a catalyst, as well as other Sm_2O_3-based systems, works most effectively at low CH_4 and O_2 concentrations: at 750 °C at an overall pressure of 1 atm, and with the ratio CH_4:O_2 = 5:2, the increase in the CH_4 concentration in the initial mixture from 5 to 40% lowers the yield of C_2 hydrocarbons from 15.6 to 7.2% as a result of the decrease in selectivity from 63.4 to 26.9%.

The oxides of other lanthanides also exhibit a higher efficiency at low reactant concentrations: in the presence of La_2O_3, a decrease in the methane pressure in the initial mixture from 313 to 132 mmHg (p_{O_2} = 8.4 and 15 mmHg respectively) increased the yield of C_2 hydrocarbons from 2.53 to 4.4%.[83]

In this respect, lanthanum aluminate, which works effectively in concentrated mixtures, is preferable:[84] at 710 °C in a 1:1 methane–air mixture, the yield of C_2 hydrocarbons was 12.5% for a methane conversion of 25.3%. A disadvantage of this catalyst is its low stability as regards temperature: it loses activity and selectivity even at 800 °C, which has been attributed to the loss of its amorphous structure.[85]

Interesting data have been obtained in studies on transition metal (Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn) oxides modified by alkali metal compounds.[86–88] Systems containing LiCl have the best catalytic properties: whereas the unmodified nickel oxide propagates only extensive oxidation, after the addition of LiCl the overall yield of C_2 hydrocarbons at 750 °C and initial CH_4 and O_2 concentrations of 5 and 2% respectively reaches 28.9% for a C_2H_4 yield of 26.2%. Under the same conditions, the yields of C_2H_4 and C_2H_6 on the 20% $LiCl/MnO_2$ catalyst are respectively 28.1 and 25%. With increase in the reactant concentrations in the initial mixture by a factor of 10, the yield of C_2 hydrocarbons falls approximately by a factor of 1.5.[85]

A serious disadvantage of the catalysts containing alkali metal halides is their rapid deactivation: LiCl containing specimens based on Sm, Ni, and Mn oxides are deactivated in several hours. There is a simultaneous decrease in the ratio C_2H_4/C_2H_6. The deactivation is attributed to the abstraction of chlorine from the catalysts, since CH_3Cl has been detected in the reaction mixture, its amount decreasing in parallel with the loss of activity.[87]

As already mentioned, in the presence of N_2O, the oxidative condensation of methane in the presence of zeolitic catalysts leads to the formation of aromatic hydrocarbons,[50,51] whereas oxidation with oxygen leads to the formation of carbon oxides.[27] Modification of zeolites with manganese promotes the manifestation by the latter of catalytic activity in the oxidative condensation of methane to C_2 hydrocarbons in the presence of O_2.[89,90] The best parameters are attained when manganese-containing catalysts based on the NaH-HSZ † ($SiO_2:Al_2O_3$ = 71) zeolite are used: at 750 °C and with the CH_4:air = 0.83 : 1 ratio, the yield of C_2 hydrocarbons is 9.5%.

Thus a whole series of catalytic systems active in the oxidative condensation of methane are now known. However, the known catalysts suffer from a number of disadvantages, which precludes their practical use:

(1) They all exhibit the optimum efficiency at high temperatures (> 700 °C), which complicates the apparatus needed for the process.

(2) The most effective catalysts work well in mixtures with low CH_4 and O_2 concentrations; as a result, even when the yields of the target products relative to the methane passed through the system are high, their concentration in the reaction mixture is low, which prevents their isolation by the known methods.[91]

(3) The activity and selectivity of many catalysts fall rapidly during their operation because of the entrainment of active components; other catalysts are unstable when overheated, which happens inevitably when the higher exothermic process considered (with a relatively low selectivity) is carried out in a large reactor.

The elucidation of the causes of the above disadvantages and the search for possible ways of eliminating them require the study of the process mechanism.

3. Hypotheses concerning the mechanism of the oxidative condensation of methane

The available literature data on the mechanism of the oxidative condensation of methane relate to the following questions: (1) the nature of the stages involving the activation of CH_4 molecules; (2) the mechanism of the formation of oxidative condensation products; (3) the nature of the active centres of the catalysts.

There exists apparently a unanimous view at the present time concerning the nature of the stage leading to the activation of the methane molecule: it involves the dissociation of a C–H bond with the simultaneous formation of a surface OH group and a methyl fragment. However, the ideas concerning the state of this fragment are different among different workers.

It has been suggested[53,67,92,93] that the CH_3 group bound to the surface is formed in the first stage. On the other hand, in a study of the interaction of CH_4-O_2 and CH_4-N_2O mixtures with catalysts of the oxidative condensation of methane at pressures less than 1 mmHg and temperatures below 450 °C, the liberation of $CH_3^{\cdot}$ radicals into the gas phase was detected by the freezing out method, which indicates the possibility of the formation of radicals not bound to the surface in this stage.[74–76,83]

The possibility of the oxidative condensation of methane via a heterogeneous-homogeneous mechanism was postulated already in one of the first studies on this process.[94] The formation of radicals under the conditions of the catalytic oxidation of methane over a wide temperature range (400–800 °C) at atmospheric pressure has been observed[95] and it has been shown that, in the presence of a more effective catalyst (10 mole % K_2O/Al_2O_3), the rate of formation of radicals is much higher than on a less effective catalyst (θ-Al_2O_3). The formation of radicals has been detected[63] by the lead mirror method in the reduction of the 15% Pb + 5% $Na_4P_2O_7/SiO_2$ system. The volume propagation of the methane oxidation process in the presence of Al_2O_3 and SiO_2 was observed even earlier by methods involving separate calorimetric measurements and the freezing out of radicals,[93] although the products in this study were oxygen-containing compounds.

If the question of pathways leading to the formation of the products of the oxidative condensation of methane in the presence of oxide systems with deposited platinum group metals is ignored,[52] then one must conclude that, according to the majority of investigators, the primary product is ethane. This is indicated by the dependence of the yield of hydrocarbons on temperature and contact time in the presence of MgO-based catalysts[77,96] and catalysts containing Bi_2O_3,[67] PbO,[68] and lanthanide oxides[81,83,84] and also by analogous data obtained in the reduction of Mn/SiO_2 systems with methane.[62,63] It has been noted[97] that the sequence in the formation of C_2 and C_3 hydrocarbons in accordance with the scheme $CH_4 \rightarrow C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2$, C_3H_6 ($\rightarrow C_3H_4$) is a general feature of the oxidative condensation of methane on oxide catalysts of different chemical nature. Similar effective activation energies for the formation of ethane—the primary condensation product—have been observed for many catalysts. It amounts to 46.5 ± 1.5 kcal mol^{-1},[98] which is extremely close to the activation energy for the formation of methyl radicals in the presence of the MgO-based catalyst (42 ± 6 kcal mol^{-1} [74]).

The approximate identity of the proportions of the hydrocarbon products in the reduction of various oxide catalysts with methane[62,63] cannot apparently serve as evidence for a heterogeneous-homogeneous process mechanism. A more convincing argument is the closeness of the rates of formation of radicals and oxidative condensation products.[74,95] The homogeneous formation of C_3 and C_4 olefins as a result of the interaction of $CH_3^{\cdot}$ radicals with ethylene and propene respectively is indicated by the sharp increase in their yield when lower olefins are added to methane used to reduce the catalysts.[62,63]

On the other hand, data have been obtained by IR spectroscopy[71] showing the formation on the surfaces of the PbO/Al_2O_3 and Li/MgO catalysts of unidentified surface compounds which can serve, according to the authors, as sources or precursors of ethylene.

† HSZ = high-silica zeolite (Ed. of Translation).

This means that there can exist a parallel pathway leading to the formation of C_2H_4. There are also data according to which methane is converted into ethylene on certain catalysts (for example, $LiCl/Al_2O_3$ [88]) without the formation of appreciable amounts of ethane. The formation of adsorbed CH_3 and CH_2 fragments as well as ethane-like structures has also been observed by Raman spectroscopy in the adsorption of methane on oxidised metallic films at low temperatures.[99]

Thus there exist two views concerning the mechanism of the formation of the products of the oxidative condensation of methane.

(1) The heterogeneous mechanism. The activation of methane is accompanied by the formation of surface CH_3 groups bound to oxygen or metal ions, for example, in the form CH_3O^- [48] or $CH_3^{\delta-}M^{\delta+}$;[67] the interaction of these groups on the surface leads to the formation of ethane, which is successively converted into ethylene. There is a possibility of the parallel formation of ethylene from the surface compounds.[71]

(2) The heterogeneous-homogeneous mechanism. The activation of methane leads to the formation of the $CH_3^{\cdot}$ free radicals (either directly or via the intermediate formation of a CH_3 group bound to the surface[70]); the recombination of the $CH_3^{\cdot}$ radicals in the gas phase results in the formation of ethane, which is successively converted into ethylene as a result of oxidative dehydrogenation on the catalyst.

The choice between these two alternative schemes is of fundamental importance both from the standpoint of the determination of the true process mechanism and from the standpoint of the creation of effective catalysts. If the heterogeneous mechanism is valid, then the catalyst should have the optimum adsorption properties, ensuring the binding of the CH_3 fragments in the necessary form and the possibility of their interaction with formation of ethane (or of its adsorbed precursor). Furthermore, the oxygen present on the catalyst surface must not be too active, so that the bound hydrocarbon fragments are not oxidised to CO and CO_2. In this case, it appears important to examine the nature of the catalyst from the standpoint of its ability to convert the CH_3 groups into electron-deficient or neutral states or states with an electron excess.[70,100] Hence follows the concept of the selection of catalysts on the basis of their acid-base properties.[101] As already mentioned, in a whole series of cases a direct correlation has been observed between the efficiency of the catalysts and their basicity.

On the other hand, according to the heterogeneous-homogeneous mechanism, the efficiency of the catalyst is determined by its ability to generate $CH_3^{\cdot}$ radicals in the gas phase. The possible homogeneous reactions leading to the formation of both the target products (the combination of $CH_3^{\cdot}$ radicals) and of oxygen-containing compounds (the interaction of methyl radicals with O_2 to form the $CH_3O_2^{\cdot}$ radicals) then becomes important for the further course of the process.[77,83,95]

The heterogeneous-homogeneous process mechanism appears more probable at the present time. It is supported by the experimental detection of radicals, formed in the oxidation of methane in the presence of various oxide catalysts, with a direct correlation of the yield of radicals and the efficiency of the catalysts, and by the similarity of the rates of formation of radicals and hydrocarbon products.

The compounds and fragments on the surfaces of catalysts, whose presence has been demonstrated by spectroscopic methods, may not in fact be precursors of the oxidative condensation products but can lead to extensive oxidation. Nor is there reliable evidence of the occurrence of the parallel process involving the formation of ethylene, because in those cases where large amounts of C_2H_4 were formed on the catalysts for a low yield of C_2H_6 the dependence of the yield of products on temperature and contact time was not stated. For low conversions, the primary hydrocarbon product on all the specimens investigated is ethane,[97] as should in fact be the case according to the heterogeneous-homogeneous scheme.

This model can explain also another general feature—the increase in selectivity with increasing temperature for low conversions. In the initial stage of the process, where the only hydrocarbon product is ethane and its successive transformations can be neglected, the set of reactions occurring in the gas phase can be reduced to the following stages:[95]

$$[O] + CH_4 \xrightarrow{k_1} [OH] + CH_3^{\cdot}, \quad (16)$$

$$2CH_3^{\cdot} \xrightarrow{k_2} C_2H_6, \quad (17)$$

$$CH_3^{\cdot} + O_2 \xrightarrow{K_3} CH_3O_2^{\cdot}, \quad (18)$$

$$2CH_3O_2^{\cdot} \xrightarrow{k_4} \text{extensive oxidation products;} \quad (19)$$

$$CH_3^{\cdot} + CH_3O_2^{\cdot} \xrightarrow{k_5} \text{extensive oxidation products.} \quad (20)$$

Analysis of this scheme on the hypothesis that equilibrium has been attained in stage (18) and that the system is quasi-stationary with respect to the sum of the radicals $CH_3^{\cdot}$ and $CH_3O_2^{\cdot}$ makes it possible to obtain an expression for the limiting selectivity S_{lim} determined solely by the processes occurring in the gas phase, provided that the catalyst surface participates only in the radical generation stage (16) and that the parallel extensive oxidation process does not take place on it:

$$S_{lim} = \left[1 + K_3 p_{O_2}\left(\frac{k_4}{k_2} K_3 p_{O_2} + \frac{k_5}{k_2}\right)\right]^{-1},$$

where p_{O_2} is the partial pressure of oxygen, K_3 is the equilibrium constant of stage (18), and k_2, k_4, and k_5 are the rate constants for stages (17), (19), and (20) respectively.

The above expression describes also the temperature dependence of S_{lim}. Since the equilibrium stage (18) shifts to the left with increase in temperature, S_{lim} increases. Experimental data have shown[95] that, on all the catalysts investigated, the observed selectivity for low conversions is below S_{lim}. This indicates the existence of a parallel channel leading to heterogeneous extensive oxidation. Analysis demonstrates that the effective activation energy for the heterogeneous extensive oxidation is as a rule lower than the activation energy for the formation of ethane, which is an additional factor promoting an increase in selectivity with increasing temperature.

There is no unanimous view in the literature concerning the nature of the active centres of the catalysts, which reflects the absence of unanimity as regards the mechanism of the methane activation stage. If it is assumed that bound CH_3 groups, forming ultimately the target products, are present on the surface, then the catalysts should exhibit bifunctionality,[67,70] namely an oxidising capacity (for the dissociation of the C—H bond) and basicity (for the prevention of an electron density deficiency at the CH_3 group). The view has also been expressed[101] that the presence of nucleophilic

(basic) centres is essential for the stabilisation of the proton and the compensation for the energy expended on the heterolytic dissociation of the C–H bond in the stage involving the activation of a CH_4 molecule; in this case the oxidation surface centres should ensure the abstraction of an electron from the CH_3^- group and its transition to an electrically neutral state.

The investigators who adhere to the heterogeneous-homogeneous mechanism[73-77,81,102-104] consider only the nature of the oxidation centres promoting the homolytic dissociation of the C–H bond. Since the oxidation centres occur in both mechanisms, we shall indicate the types of such centres discussed in the literature:

Oxygen bound to readily reducible cations;[53] the participation of oxygen of this type in the process is indicated by the possibility of obtaining oxidative condensation products both under the conditions of alternate oxidation-reduction and under the conditions of continuous catalysis on the same systems.

Oxygen ions O^- existing in the form of the ion pairs M^+O^- (M^+ is an alkali metal ion) in catalysts based on alkaline earth metal oxides modified by alkali metal cations;[73-78] the formation of centres of this type becomes possible in alkaline earth metal oxides as a result of the thermally activated electron transfer from the oxygen anion to the metal cation or due to the presence of a vacancy at a neighbouring cationic site;[74,76] the presence of O^- centres has been postulated also in Sm_2O_3.[81]

O^{2-} ions with reduced coordination in lead, bismuth and magnesium oxide:[76] it may be that centres of this type are identical with the first two types both in PbO and Bi_2O_3,[53] on the one hand, and in the case of alkaline earth metal oxides,[105] on the other.

The peroxide ions O_2^{2-},[98,103,104] which may be stabilised in systems containing alkali and alkaline earth metal cations with large ionic radii.[106]

By analogy with the gas-phase process

$$O^- + CH_4 \rightarrow OH^- + CH_3, \qquad (21)$$

which occurs at a high rate even at room temperature, it has been suggested that the activation energy for a reaction of this type with participation of the O^- ions of the Li/MgO catalyst surface is also low.[77] The high observed activation energy for the formation of ethane (55 ± 1.6 kcal mol^{-1}) and the increase in selectivity with increase in temperature associated with it have been explained by the difficulty of reactivating the surface centre via the scheme:

$$\begin{aligned} &2Li^+{-}OH^- \rightarrow Li^+{-}O^{2-} + Li^+{-}[*] + H_2O, \\ &Li^+{-}O^{2-} + Li^+{-}[*] + \tfrac{1}{2}O_2 \rightarrow 2Li^+{-}O^- \end{aligned} \qquad (22)$$

or

$$\begin{aligned} &2Li^+{-}OH^- \rightarrow Li^+{-}O^- + Li^+{-}[*]^- + H_2O, \\ &Li^+{-}[*]^- + \tfrac{1}{2}O_2 \rightarrow Li^+{-}O^-, \end{aligned} \qquad (23)$$

where [*] is an oxygen vacancy and $[*]^-$ an oxygen vacancy with a captured electron.

However, this scheme does not agree with the phenomenon, observed by the same workers,[74,75] of the decay of the radical formation process via reactions of types (16) when N_2O is used as the oxidant (in the presence of O_2, there is no decay), because the filling of the oxygen vacancies, formed as a result of the dehydroxylation via schemes (22) and (23), should occur in the presence of N_2O at least no less effectively than in the presence of O_2.

The difficulty of the reoxidation of N_2O is also indicated by the data of Otsuka and Hatano:[107] when O_2 as the oxidant is replaced by N_2O, the conversion of CH_4 in the presence of the Sm_2O_3 catalyst decreases significantly. At the same time, the selectivity at relatively low temperatures (below 680 °C) increases in the presence of N_2O, which is fully explicable within the framework of the heterogeneous-homogeneous mechanism, since the extensive oxidation processes in the gas phase proceed via the $CH_3O_2^{\cdot}$ radicals whose formation is impossible in the absence of molecular oxygen.

As regards the basicity of the catalyst, an alternative explanation of its influence on their efficiency in the oxidative condensation of methane is apparently possible. It has been shown[108] that one of the pathways leading to the formation of the extensive oxidation products may be the decomposition of formaldehyde via the reaction

$$CH_2O \rightarrow CO + H_2. \qquad (24)$$

As already mentioned, the formation of CH_2O in the oxidation of methane takes place most effectively on catalysts with a high acidity.[30-33] The increase in selectivity with respect to hydrocarbons after the introduction of alkaline additives can then be attributed to the decreased contribution of this extensive oxidation channel as a result of the suppression of the acid centres.[68]

Together with the increase in selectivity, after the introduction of alkali and alkaline earth metal cations, an increase in the rate of formation of the products of the oxidative condensation of methane is also observed.[72,98,102] This is associated with the increase in the amount of the active forms of oxygen, for example O^- (in alkaline earth metal oxides with alkali metal additives[73-78]) or O_2^{2-} (in the M_2O/Al_2O_3 [97] and BaO [103,104] systems). Whereas the efficiency of the M_2O/Al_2O_3 catalysts increases under these conditions with increase in the ionic radius of the alkali metal cation,[97,102] the opposite variation is observed for the M_2O/MgO and M_2O/CaO systems,[77,102] which can be readily explained by the influence of the alkali metal cation on the properties of the oxygen of the catalysts. Thus the observed relation between basicity and catalyst efficiency can be purely superficial and may not be determined by the involvement of the basic centres directly in the stage involving the activation of CH_4 molecules. The final elucidation of this question requires additional research.

4. Kinetics of the oxidative condensation of methane

Some light may be thrown on the mechanism of the process by studying its kinetics. Unfortunately, one should note that, on the majority of the catalysts described in the literature, the kinetics of the oxidative condensation of methane have not been studied. The 7% Bi_2O_3–9% K_2CO_3/Al_2O_3 [67] and 34% PbO/Al_2O_3 [68] systems are an exception. Formal power equations of the following type were used for the kinetic description in both cases:

$$r_i = k_i p_{hc}^m p_{O_2}^n, \qquad (25)$$

where r_i is the rate of the ith process, k_i the observed rate constant, p_{hc} and p_{O_2} are the hydrocarbon and oxygen pressures respectively, and m and n are the effective reaction orders with respect to carbon and oxygen respectively.

The kinetic parameters obtained in the above studies[67,68] are listed in Table 1.

The kinetic parameters quoted in these studies[67,68] have been scarcely discussed apparently because of their formal character and low information content. The activation energies for the formation of CO, determined by Hinsen et al.,[68] illustrate qualitatively the observed increase in selectivity in the temperature range up to 700–750 °C without, however, any explanation of this finding.

Table 1. Kinetic parameters of the overall stages of the oxidative condensation of methane on the 7% $Bi_2O_3-K_2CO_3/Al_2O_3$ (I) [67] and 20% PbO/Al_2O_3 (II) [68] catalysts.

Stage	Catalyst					
	I				II	
	m	n	m	n	E, kcal mol^{-1}	k_i
$CH_4 \rightarrow C_2H_6$	2	1	1.1±0.3	0.8±0.2	24	$6.0\cdot10^4$
$CH_4 \rightarrow CO_2$	0.3	1	1.5±0.3	0.4±0.1	12	$1.5\cdot10^6$
$C_2H_6 \rightarrow C_2H_4$	1	2.5	1±0.2	0.8±0.1	1.5	$1\cdot10^2$
$C_2H_6 \rightarrow CO_2$	0	1.4	—	—	—	—
$C_2H_4 \rightarrow CO_2$	0	0.6	1.6±0.3	0.8±0.3	−52	$1\cdot10^{-10}$

The kinetics of the oxidation of methane on the 20% PbO/Al_2O_3 catalyst have been studied in detail.[95,104] For low conversions, taking into account the contribution of the homogeneous stages, the rate of the process in the ethane formation pathway is described by the kinetic equation characteristic of processes occurring via an oxidation-reduction mechanism:

$$r_1 = \frac{k_r p_{CH_4} k_{ox} p_{O_2}}{k_r p_{CH_4} + k_{ox} p_{O_2}}, \quad (26)$$

where k_r and k_{ox} are the rate constants for the reduction of the active centres by methane and for their reoxidation by oxygen respectively and p_{CH_4} and p_{O_2} are the methane and oxygen pressures respectively.

The kinetics of the conversion of ethane into ethylene on this catalyst are described by an analogous equation, which can be obtained on the assumption that two oxidised centres participate in the process:

$$r_2 = \frac{4k_r' p_{C_2H_6} k_{ox}^2 p_{O_2}^2}{(k_{ox} p_{O_2} + (k_{ox}^2 p_{O_2}^2 + 8k_r' p_{C_2H_6} k_{ox} p_{O_2})^{-1/2})^2}, \quad (27)$$

while k_r' is the rate constant for the reduction of the active centres by ethane and $p_{C_2H_6}$ is the ethane pressure.

The reoxidation rate constants, found in experiments with methane and ethane, proved to be extremely close, from which it was concluded that the same active centres are involved in both processes. The rate constants for the interaction of ethane with oxidised active centres were 10–20 times higher at identical temperatures than the corresponding constants for methane. From the pre-exponential factor for the constant k_r (assuming the impact character of the reduction stage), it was found that the surface concentration of the active centres is 0.3% of a monolayer on the catalyst surface.

Analysis of Eqn. (26) made it possible to explain the similarity of the effective activation energies E_{eff} for the formation of ethane on different catalysts.[95] It was shown that the following expression is valid for E_{eff}:

$$E_{eff} = \frac{\kappa E_r + E_{ox}}{1 + \kappa} \quad (28)$$

where E_r and E_{ox} are the activation energies for reduction and reoxidation respectively and $\kappa = k_{ox} p_{O_2} / k_r p_{CH_4}$.

For κ not differing greatly from unity, E_{eff} is close to half the sum of E_r and E_{ox}. On the other hand, if E_{ox} increases linearly with decrease in E_r, then E_{eff} is approximately constant in the series of catalysts. When one of the processes—reduction or reoxidation—takes place at a significantly lower rate than the other, the rate of the overall process is naturally determined by the kinetic parameters of the slower stage. Thus it has been shown[104] that in the case of BaO the reoxidation stage is slow which induces an increase in E_{eff} to a value in excess of 60 kcal mol^{-1}.

According to Sinev et al.,[98] the rates of the extensive oxidation of methane and ethane on the 20% PbO/Al_2O_3 catalyst are described by kinetic equations of the Langmuir type, which indicates the involvement of adsorbed forms in the reaction. This means that the mechanisms of the oxidative condensation and extensive oxidation differs significantly.

5. Reactions of methane on photoactivated and mechanically activated oxides

Additional information about the mechanism of the process considered has been obtained in studies on oxide systems subjected to photochemical[109–114] and mechanochemical[115–118] activation.

The action of radiation (in the visible, UV, X-ray, and γ-ray ranges) on TiO_2 [109–111] and other simple oxides[112,114] and also on SiO_2 and Al_2O_3 modified by vanadium and molybdenum ions[109,113] leads to the photosorption of methane. When the system is heated, C_2 and C_3 hydrocarbons as well as CH_3OH and C_2H_5OH appear in considerable amounts in the thermal desorption spectrum in addition to methane and carbon oxides. A certain amount of other hydrocarbons can be collected in a cooled trap even when methane is passed over photoactivated specimens at room temperature,[110] which indicates an extremely low activation energy for their formation. The principal characteristics of the photostimulated condensation of methane have been formulated by Kotova.[114]

(1) In the photoreactions of methane on oxides, two competing processes occur simultaneously: the formation of hydrocarbons and the formation of oxygen-containing compounds. On irradiation in the region of the intrinsic absorption by the oxide, the second process predominates, while outside this region (in the region where the defects absorb) the first process is dominant.

(2) The first stage of the process is homolytic dissociation of the C–H bond; the dissociative adsorption of hydrocarbons is accompanied by the formation of excited surface OH groups.

(3) After a time, the surface is poisoned by the reaction products and the efficiency of the photoconversion of methane decreases; the surface can be regenerated by a high-temperature treatment in oxygen.

(4) The presence of H_2 and O_2 in the system decreases the yield of hydrocarbons.

(5) There exist analogous dark reactions of methane, which may indicate the similarity of the mechanisms of the dark conversion and photoconversion of methane. It has been suggested that weakly coordinated oxygen ions in a charged state close to −1, whose properties are analogous to those of photoinduced hole O^- centres, participate in the dark process.

Thus data on the photoreactions of methane also indicate the involvement of weakly coordinated oxygen of the oxides and centres of type O^- in its activation. The direct use of these data for the description of the mechanism of the catalytic oxidative condensation of methane is precluded by the fact that, among the systems investigated in photostimulated processes, only La_2O_3 is effective in the usual catalytic reaction.[83] The dark reactions of methane leading to its conversion into other hydrocarbons have been observed on Ga_2O_3, SnO_2, and α- and η-Al_2O_3,[114] which are poor catalysts of oxidative condensation. Furthermore, the postulated intermediate carbon-containing compounds have not been detected experimentally and the mechanisms discussed are hypothetical.

The study of the centres formed on oxides surfaces disordered by mechanical activation (in the first place on SiO_2 and GeO_2 [115–118]) has shown that some of them are very highly reactive in relation to molecule such as those of H_2 and lower paraffins and are capable of inducing the dissociation of H−H and C−H bonds. Such centres include strained Si−O−Si bridges, the radical centres $-\overset{\diagdown}{\underset{\diagup}{\dot{S}i}}$, $-\overset{\diagdown}{\underset{\diagup}{SiO^{\cdot}}}$, and $-\overset{\diagdown}{\underset{\diagup}{SiOO^{\cdot}}}$,[117] as well as groups of the peroxide type $-\overset{\diagdown}{\underset{\diagup}{Si}}-O-O-\overset{\diagup}{\underset{\diagdown}{Si}}-$.[118] The interaction of methane with these centres proceeds via reactions of type (16), the oxy-radicals $SiO^{\cdot}$ and $-\overset{\diagdown}{\underset{\diagup}{GeO^{\cdot}}}$ (in the case of GeO_2) being most active. The $CH_3^{\cdot}$ radicals are formed on them with an exothermic effect of 14–17 kcal mol^{-1} and an activation energy close to.[117] The methyl fragments formed are bound to centres of different types, present in a large amount on the mechanically activated surface (=Si:, $-\overset{\diagdown}{\underset{\diagup}{SiOO^{\cdot}}}$, $-\overset{\diagdown}{\underset{\diagup}{Si}}-O-\overset{\diagup}{\underset{\diagdown}{Si}}-$, $-\overset{\diagdown}{\underset{\diagup}{Si}}-O-O-\overset{\diagup}{\underset{\diagdown}{Si}}-$) and undergo further reactions (more far reaching dehydrogenation and decomposition accompanied by isomerisation[117]). It is notable that methyl radicals have also not been detected in these investigations, although the authors identified by EPR a series of paramagnetic products of their interaction with various surface centres (=$SiCH^{\cdot}$, $-\overset{\diagdown}{\underset{\diagup}{SiCH_2^{\cdot}}}$, $-\overset{\diagdown}{\underset{\diagup}{SiOCH_2^{\cdot}}}$).

Unfortunately the centres formed on mechanically disordered surfaces are thermally unstable (because of their non-equilibrium nature) and are annealed at lower temperatures than those at which oxidative condensation of methane takes place. This factor as well as the absence of information in the relevant communications[115–118] about the hydrocarbon methane conversion products necessitates some caution in using the above data for the description of the mechanism of the oxidative condensation.

The mechanism of the formation of C_2 hydrocarbons in the presence of oxides modified by alkali metal halides apparently appears to be somewhat different.[82,86–88] However, in this case too a heterogeneous-homogeneous process is most likely with the participation of an atomic halogen, for example chlorine, in the initiation stages:

$$Cl + CH_4 \rightarrow HCl + CH_3^{\cdot}, \quad (29)$$

$$Cl + C_2H_6 \rightarrow HCl + C_2H_5^{\cdot}. \quad (30)$$

Chlorine atoms can be formed both in the decomposition of Cl_2 molecules formed via the Deacon reaction

$$2HCl + O_2 \rightarrow H_2O + Cl_2, \quad (31)$$

and in the direct oxidation of the alkali metal chloride melt on the oxide surface. The possibility of the oxidative condensation of methane via the oxidation of halides analogously to the hydroxychlorination of hydrocarbons is indicated by the high efficiency of the same transition metal oxides with added alkali metal halid salts in both reactions.

At high temperatures and appreciable concentrations of water in the reaction mixture, the reversible hydrolysis of the halides (for example, LiCl), i.e.

$$2LiCl + H_2O \rightleftharpoons Li_2O + 2HCl \quad (32)$$

can maintain the optimum concentration of HCl in the system, ensuring both its supply to the gas phase in order to effect reaction (31) and its binding, which precludes its being carried away from the reaction zone. However, at high concentrations of the $CH_3^{\cdot}$ radicals and $Cl^{\cdot}$ atoms, there is a high probability of the reaction

$$CH_3^{\cdot} + Cl^{\cdot} \rightarrow CH_3Cl, \quad (33)$$

which leads to the active component being carried away and to the loss of catalytic activity.[88]

- - - o 0 o - - -

The available literature data on the reactions leading to the conversion of methane into methanol, formaldehyde, and hydrocarbons, including unsaturated and aromatic hydrocarbons, show that heterogeneous-catalytic processes constitute the most promising method for the conversion of methane into intermediate products of organic and petrochemical synthesis.

Many oxide systems exhibit catalytic activity in the oxidative condensation of methane to other hydrocarbons. However, virtually all the known catalysts suffer from the same disadvantages, which preclude the practical realisation of the process. The most effective catalysts afford the maximum yield of the target products at 700–750 °C, i.e. at an extremely high temperature.

According to its nature, the process is heterogeneous-homogeneous, which may lead to an appreciable influence of the reactor material and its parameters, especially at high temperatures. The highest yields of C_2 hydrocarbons have been observed, as a rule, in quartz reactors. The practical realisation of the process necessitates the use of metallic reactors and it is to be expected that at temperatures of 600 °C and above the rate of the extensive oxidation of methane will increase under the influence of the reactor material and hence selectivity will fall appreciably.[53]

This difficulty can be overcome, on the one hand, by creating highly efficient catalysts capable of propagating the process at lower temperatures and, on the other hand, by suppressing the activity of the reactor walls with respect to the extensive oxidation of methane.

The problem of the increase in the volume concentration of the products of the oxidative condensation of methane, which would greatly facilitate the task of their isolation and would increase the economic effectiveness of the process, is no less important. It is therefore necessary to achieve the stable operation of the catalyst at a high concentration of the reactant in the initial mixture.

The use of oxide systems, in which lattice oxygen exhibits a high mobility and activity, may prove promising. The oxidative condensation of methane on such catalysts under the conditions of alternate reduction-oxidation would permit the attainment of the maximum possible volume concentrations of useful products.

Despite the complexity of the catalytic activation of methane, the advances achieved in this field, especially as regards the oxidative condensation of methane, permit one to hope that practical solution to the problem will be found in the near future. This will be assisted by broadening the research into the mechanism and kinetics of the catalytic oxidation of methane.

References

1. V A Legasov, A L Buchachenko *Uspekhi Khim.*, 1986, **61**(11) 1937 [*Russ. Chem. Rev.*, 1986(11)]
2. B N Kuznetsov *Izv. Sibir. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk*, 1987, (4) 117
3. S F Evanlov, N V Lavrov *Nauchnye Osnovy Kataliticheskoi Konversii Uglevodorov* (Scientific Principles of the Catalytic Conversion of Hydrocarbons), Izd. Naukova Dumka, Kiev, 1977, p. 210
4. R Z Magaril *Mekhanizm i Kinetika Gomogennykh Termicheskikh Prevrashchenii Uglevodorodov* (The Mechanisms and Kinetics of the Homogeneous Thermal Reactions of Hydrocarbons), Izd. Khimiya, Moscow, 1970
5. H D Gesser, N R Hunter, C B Prakash *Chem. Rev.*, 1985, **85** 235
6. Yu M Zhorov *Termodinamika Khimicheskikh Protsessov* (Thermodynamics of Chemical Processes), Izd. Khimiya, Moscow, 1985
7. J M Roscoe, M J Thompson *Int. J. Chem. Kinet.*, 1985, **17** 967
8. C-J Chen, M H Back, R A Back *Canad. J. Chem.*, 1975, **53** 3580
9. C-J Chen, M H Back, R A Back *Canad. J. Chem.*, 1976, **54** 3175
10. N M Emanuel' *Promezhutochnye Produkty Slozhnykh Gazovykh Reaktsii* (Intermediates in Complex Gas Reactions), Izd. Akad. Nauk SSSR, Moscow, 1946
11. A I Suleimanov, S M Aliev, V D Sokolovskii *React. Kinet. Catal. Lett.*, 1986, **31** 285
12. N N Semenov *O Nekotorykh Problemakh Khimicheskoi Kinetiki i Reaktsionnoi Sposobnosti* (Some Problems of Chemical Kinetics and Reactivity), Izd. Akad. Nauk SSSR, Moscow, 1958
13. L V Karmilova, N S Enikolopyan, A B Nalbandyan, N N Semenov *Zhur. Fiz Khim.*, 1960, **34**(6) 1176 [*Russ. J. Phys. Chem.*, 1960(6)]
14. I A Vardanyan, S Yan, A B Naldandyan *Kinetika i Kataliz*, 1981, **22** 845
15. V Ya Basevich, S M Kogarko *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1982, (12) 2658
16. A A Borisov, E V Dragalova, V M Zamanskii, et al. *Kinetika i Kataliz*, 1981, **22** 305
17. D J Huckal *Chemistry of Hydrocarbons Combustion*, Chapman and Hall, London–New York, 1985
18. A A Mantashyan, A B Nalbandyan *Zhur. Fiz. Khim.*, 1972, **46**(12) 3030 [*Russ. J. Phys. Chem.*, 1972(12)]
19. V N Kondrat'ev *Konstanty Skorosti Gazofaznykh Reaktsii* (The Rate Constants for Gas-phase Reactions), Izd. Nauka, Moscow, 1970
20. K Hoyerman, H G Wagner *Oxid. Comm.*, 1982, **2** 259
21. W B Demore, J J Magiton, M J Molina, et al *Int. J. Chem. Kinet.*, 1985, **17** 1135
22. W Tsang, R F Hampson *J. Phys. Chem., Ref. Data*, 1986, **15** 1086
23. V E Leonov, V E Limonov, A D Khaitun, I V Krupnik *Khim. Prom. za Rubezhom*, 1976, (5) 33
24. L F Marek, D A Gan *Kataliticheskoe Okislenie Organicheskikh Soedinenii* (Catalytic Oxidation of Organic Compounds), Izd. ONTI, Moscow, 1936
25. V A Roiter (Editor), Handbook *Kataliticheskie Svoistva Veshchestv* (Catalytic Properties of Substances), Izd. Naukova Dumka, Kiev, 1968
26. G K Boreskov, V A Sazonov, V V Popovskii *Dokl. Akad. Nauk SSSR*, 1967, 176
27. S S Shepelev, K G Ione *React. Kinet. Catal. Lett.*, 1983, **23** 323
28. Yu L Vysotskii, L E Semikina, Ya A Shuster, et al. *Kataliz i Katalizatory*, 1979, (17) 82
29. V E Leonov, L M Kalinichenko, Yu V Shulyakov, et al. *Kataliz i Katalizatory*, 1977, (15) 6
30. V A Borko, V I Gomonai, K Yu Sekeresh *Soobshch. po Kinetike i Katalizu*, 1980, **14** 439
31. B M Ershov, K Yu Sekeresh, I I Gusinka, M A Pueva *Izuchenie Protsessa Okisleniya Metana na Kislotno-Osnovnykh Katalizatorakh* (The Oxidations of Methane on Acid–Base Catalysts), Deposited at the ONIITEKhIM, Cherkassy, 1.12.82, No. 1273KhP-D82
32. USSR P. 958 407; *Byul. Izobret.*, 1982, (7)
33. V I Gomonai, D I Mel'nik, and K Yu Sekeresh *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Mekhanizmu Kataliticheskikh Reaktsii* (Abstracts of Reports of the IVth All-Union Conference on the Mechanisms of Catalytic Reactions), Moscow, 1986, Part 2, p. 72
34. A Ya Averbukh, N Yu Pavlova *Geterogennye Kataliticheskie Protsessy* (Heterogeneous Catalytic Processes), Leningrad, 1979, p. 94
35. Yu A Ivanov, A Ya Averbukh, I P Mukhlenov, L I Musienko *Tezisy Dokladov IV Respublikanskoi Konferentsii po Okislitel'nomu Geterogennomu Katalizu* (Abstracts of Reports at the IVth Republican Conference on Oxidative Heterogeneous Catalysis), Baku, 1978, Part 2, p.56
36. USSR P. 366 178; *Byul. Izobret.*, 1973, (7)
37. R S Mann, M K Dosi *J. Chem. Techn. Biotechnol*, 1979, **29** 467
38. L A Nersesyan, Candidate's Thesis in Chemical Sciences, Institute of Chemical Physics, Academy of Sciences of the Armenian SSSR, Erevan, 1979
39. *Appl. Catal.*, **26** 408
40. M Iwamoto, S Kagawa, J H Lunsford *Shokubai (Catalyst)*, 1981, **23** 278
41. M Iwamoto *MOL*, 1982, 79
42. H-P Liu, R-S Liu, K J Liew, et al. *J. Amer. Chem. Soc.*, 1984, **106** 4117
43. R-S Liu, M Iwamoto, J H Lunsford *J. Chem. Soc., Chem. Comm.*, 1982, 78

44. K Aika, J H Lunsford *J. Phys. Chem.*, 1977, **84** 1393
45. M M Khan, G A Somorjai *J. Catal.*, 1985, **91** 263
46. M Inokawa, K Mori, A Miyamoto, Y Murakami, *J Phys. Chem.*, 1983, **87** 761
47. K J Zhen, M M Khan, S H Mak, et al. *J. Catal.*, 1985, **94** 501
48. F Solymosi, I Tombacz, G Kutsan *J. Chem. Soc., Chem. Comm.*, 1985, (20) 1455
49. T S Seiyama *Oxid. Comm.*, 1982, **2** 239
50. S S Shepelev, Abstract of Candidate's Thesis in Chemical Sciences, Institute of Kinetics [and Organic Synthesis], Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1987
51. S S Shepelev, K G Ione *React. Kinet. Catal. Lett.*, 1983, **23** 319
52. US P. 4 205 194, 1980
53. G F Keller, M M Bhasin *J. Catal.*, 1982, 73 9
54. US P. 4 554 395, 1985
55. US P. 4 544 786, 1985
56. US P. 4 547 608, 1985
57. US P. 4 547 607, 1985
58. US P. 4 547 611, 1985
59. B. P. 2 156 842, 1985
60. US P. 4 544 784, 1985
61. US P. 4 517 398, 1985
62. J A Sofranko, J J Leonard, C A Jones *J. Catal.*, 1987, **103** 302
63. C A Jones, J J Leonard, J A Sofranko *J. Catal.*, 1987, **103** 311
64. US P. 4 523 049, 1985
65. US P. 4 547 610, 1985
66. *Appl. Catal.*, 1986, **27** 410
67. I T Ali Emesh, Y Amenomiya *J. Phys. Chem.*, 1986, **90** 4785
68. W Hinsen, W Bytyn, M Baerns *Proceedings of VIIIth International Congress on Catalysis*, Verlag Chemie, West Berlin, 1984, Vol. III, p. 581
69. K Asami, S Hashimoto, T Shikada, et al. *Chem. Lett.*, 1986, 1233
70. K Asami, S Hashimoto, T Shikada, et al. *Ind. Eng. Chem. Res.*, 1986, **26** 1485
71. J A Roos, A G Bakker, H Bosch, et al. *Catalysis Today*, 1987, **1** 133
72. N P Kirik, A G Anshits, A S Ivanova *Khimicheskii Sintez na Osnove Odnouglerodnykh Molekul. Tezisy Dokladov Vsesoyusnogo Soveshchaniya* (Chemical Synthesis Based on One-carbon Molecules. Abstracts of Reports at an All-Union Conference), Izd. Nauka, Moscow, 1984, p. 75
73. T Ito, J H Lunsford *Nature (London)*, 1985, **314** 721
74. D J Driscoll, W. Martir, J-X Wang, J H Lunsford *J. Amer. Chem. Soc.*, 1985, **107** 48
75. D J Driscoll, W Martir, J-X Wang, J H Lunsford *Adsorption and Catalysis on Oxide Surfaces*, Amsterdam, 1985, p. 403
76. D J Driscoll, J H Lunsford *J. Phys. Chem.*, 1985, **89** 4415
77. T Ito, J-X Wang, C-X Lin, J H Lunsford *J. Amer. Chem. Soc.*, 1985, **107**
78. J-X Wang, J H Lunsford *J. Phys. Chem.*, 1986, **90** 5883
79. T Moriyama, N Takasaki, E Iwamatsu, K Aika *Chem. Lett.*, 1986, 1165
80. K Otsuka, K Jinno, A Morikawa *Chem. Lett.*, 1985, 499
81. K Otsuka, K Jinno, A Morikawa *J. Catal.*, 1986, **100** 353
82. K Otsuka, Q Liu, M Hatano, A Morikawa *Chem. Lett.*, 1986, 467
83. C-H Lin, K D Campbell, J-X Wang, J H Lunsford *J Phys. Chem.*, 1986, **90**
84. H Imai, T Tagawa *J Chem. Soc., Chem. Comm.*, 1986, (1) 52
85. H Imai, T Tagawa, N Kamide *Proceedings of VIIIth Japan–USSR Catalysis Seminar*, Tokyo, 1986, p. 139
86. K Otsuka, Q Liu, M Hatano, A Morikawa *Chem. Lett.*, 1986, 903
87. K Otsuka, Q Liu, A Morikawa *Inorg. Chim. Acta*, 1986, **118** L23
88. K Otsuka, M Hatano, Q Liu, A Morikawa *Proceedings of VIIIth Japan–USSR Catalysis Seminar*, Tokyo, 1986, p. 1
89. Kh M Minachev, N Ya Usachev, Yu S Khodakov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, (7) 1686
90. Kh M Minachev, N Ya Usachev, Yu S Khodakov, et al. *Izv. Akad Nauk SSSR, Ser. Khim.*, 1987, (3) 504
91. R Scholler, U Muller *Chem. Techn. (DDR)*, 1986, **38** 19
92. W Bytyn, M. Baerns *Appl. Catal.*, 1986, **28** 199
93. L A Nersesyan, I A Vardanyan, E N Kegeyan, et al. *Dokl. Akad. Nauk SSSR*, 1975., **220** 605
94. T Fang, C Yeh *J. Catal.*, 1981, **69** 227
95. M Yu Sinev, Candidate's Thesis in Chemical Sciences, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1987
96. A I Suleinmanov, S M Aliev, V D Sokolovskii *Okislitel'naya Degidromerizatsiya Metana v Vysshie Uglevodorody na Mg-soderzhashchikh Katalizatorakh* (Oxidative Dehydrodimerisation of Methane to Higher Hydrocarbons on Mg-containing Catalysts), Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 11.10.85, No. 7220-V85
97. M Yu Sinev *Tezisy Dokladov III Vsesoyuznoi Konferentsii Molodykh Uchenykh po Fizicheskoi Khimii* (Abstracts of Reports at the IIIrd All-Union Conference of Young Scientists of Physical Chemistry), Moscow, 1986, p. 121
98. M Yu Sinev, V N Korchak, O V Krylov *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Meckanizmu Kataliticheskikh Reaktsii* (Abstracts of Reports at the IVth All-Union Conference on the Mechanisms of Catalytic Reactions), Moscow, 1986, Part 2, p. 27
99. S E Plate, A V Bobrov, A A Kadushin, Ya M Kimmel'fel'd *Kinetika i Kataliz*, 1986, **27** 495
100. E A Mamedov, V P Vislovskii, R G Rizaev *Kinetika i Kataliz*, 1986, **27**
101. V D Sokolovskii *React. Kinet. Catal. Lett.*, 1986, **32** 159
102. M Yu Sinev, P A Shiryaev, V N Korchak, O D Krylov *V Neftekhimicheskii Simpozium Sotsialisticheskikh Stran. Burgas (NRB)* [The Vth Petrochemical Symposium of Socialist Countries, Burgas, Bulgaria], 1986, p. 101
103. M Yu Sinev, V N Korchak, O V Krylov *Kinetika i Kataliz*, 1986, **27**
104. M Yu Sinev, V N Korchak, O V Krylov *Proceedings of the VIth International Symposium on Heterogeneous Catalysis*, Sofia, 1987, Part 1, p. 450
105. H Hattori *Adsorption and Catalysis on Oxide Surfaces* Amsterdam, 1985, p. 319
106. V I Vol'nov *Perekisnye Soedineniya Shchelochnozemel'nykh Metallov* (Peroxide Compounds of Alkaline Earth Metals), Izd. Nauka, Moscow, 1982
107. K Otsuka, M Hatano *J. Chem. Soc., Faraday Trans. I*, 1987, **83** 1315
108. M Yu Sinev, G A Vorob'eva, V N Korchak *Kinetika i Kataliz*, 1986, **27**
109. S L Kaliaguine, B N Shelimov, V B Kazansky *J. Catal.*, 1978, **55** 384

110. G N Kuz'min, M V Knatko, S V Kurganov *Tezisy Dokladov I Vsesoyuznoi Konferentsii po Kataliticheskomu Preobrazovaniyu Solnechnoi Energii* (Abstracts of Reports at the Ist All-Union Conference on the Catalytic Transformation of Solar Energy), Novosibirsk, 1983, p. 120
111. G E Kuzmin, M V Knatko, S V Kurganov *React. Kinet. Catal. Lett.*, 1983, **23**
112. V M Yurkin, Abstract of Candidate's Thesis in Physical-mathematical Sciences, Leningrad State University, Leningrad, 1985
113. S F Gerasimov, Abstract of Candidate's Thesis in Physical-mathematical Sciences, Leningrad State University, Leningrad, 1986
114. O D Kotova, Abstract of Candidate's Thesis in Physical-mathematical Sciences, Leningrad State University, Leningrad, 1986
115. V A Radtsig *Kinetika i Kataliz*, 1979, **20**, 450
116. A V Bystrikov, A N Streletskii, P Yu Butyagin *Kinetika i Kataliz*, 1980, **21** 1013
117. A A Bobyshev, V A Radtsig *Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Mechanizu Kataliticheskikh Reaktsii* (Abstracts of Reports at the IVth All-Union Conference on the Mechanisms of Catalytic Reactions), Moscow, 1986, Part 2, p. 425
118. A A Bobyshev, V A Radtsig *Khim. Fiz.*, 1986, **5** 517