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Oxidative Condensation of Methane—a New Pathway to the Synthesis of Ethane, Ethylene, and Other Hydrocarbons

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During the last five years, the chemistry of methane has been enriched by the possibility of obtaining C_2 and other hydrocarbons as a result of the oxidative condensation of methane in the presence of a series of catalytic systems. The availability of the starting materials (CH_4 and O_2) leads to extensive prospects for the replacement of the petroleum raw materials by natural gas in single-stage syntheses of valuable compounds and in the first place ethylene. This review gives a systematic account of the results of the selection of effective catalysts and surveys the information leading to the elucidation of the mechanism for the formation of the products of the extensive oxidation and oxidative condensation of methane. The bibliography includes 118 references.

CONTENTS

I. Introduction 221
II. Catalysts of the oxidative condensation of methane 221
III. The mechanism of the oxidation reactions of methane 227

I. INTRODUCTION

Methane has long attracted the attention of chemists as the starting material for the synthesis of valuable products,[1] but its high stability hinders its processing.[2] At the present time the bulk (more than 90%) of the natural gas extracted is used as fuel, although there exist industrial methods for the conversion of methane into a synthesis gas, chloro-derivatives, and acetylene.[3] The activation of CH_4 molecules, for example, for the manufacture of acetylene, is achieved at high temperatures (about 1500 °C),[1] which is due to the thermodynamic factors governing this process.

In connection with the problem of involving methane in chemical reactions studies[4-6] on its activation under comparatively mild conditions by transition metal complexes are of considerable interest. Thus at 90–120 °C and a methane pressure of 100 atm, methane is oxidised in an aqueous solution of $PtCl_4^{2-}$ and $PtCl_6^{2-}$ to CH_3OH and CH_3Cl with stoichiometric reduction of platinum(IV) to platinum(II).[4] Studies[6] on the oxidation reactions of methane under the influence of oxygen, especially its oxidation to methanol and formaldehyde, have a clear-cut practical purpose.[6] In the presence of one of the most active molybdenum-containing catalysts at 450 to 500 °C and a pressure of 50 atm, the yields of CH_3OH and CH_2O relative to the methane which has reacted reach 50–75% and 4–8% respectively for an overall conversion of methane up to 3.5%. Methods for the gas-phase oxidation of methane by atmospheric oxygen with added initiators (nitrogen oxides) are also known,[6] but the low yield of the target products hinders their practical application. In order to increase the selectivity of the formation of methanol and formaldehyde, it has been suggested[6] that N_2O be used as the oxidant, which makes it possible to avoid the extensive oxidation of methane, although the degree of conversion of the latter does not then increase and amounts to ~2%.

In the oxidation of methane with N_2O in the presence of high-silica zeolites, the formation of aliphatic and aromatic hydrocarbons is observed at a reaction temperature of 300 to 600 °C.[7-12] The dependence of the yield of hydrocarbons of different classes on temperature and on the degree of elimination of metal cations from zeolites shows that methanol, the primary methane oxidation product,[8] undergoes reactions characteristic of catalysis by high-silica zeolite (HSZ).[7] It is noteworthy that the replacement of N_2O by oxygen under the same conditions leads to the formation of the products of the extensive oxidation of methane.[8] Studies[13-15] on the oxidative coupling of methane to substances whose molecules contain methyl groups (toluene, acetonitrile) are of interest; this results in the formation of vinyl derivatives (styrene, acrylonitrile). As in the previous case, oxygen-containing methane oxidation products (CH_3OH, CH_2O) probably enter into the coupling reaction, but their yield is unfortunately low.

A new aspect of the methane chemistry arose as a result of studies by Mitchell[16-18] and Keller and Bhasin[19] in which C_2 and other hydrocarbons were detected after methane had been allowed to come into contact with the oxides of a number of metals at temperatures above 600 °C. The formation of, for example, ethane under these conditions takes place via the oxidative condensation of methane:

$$2CH_4+[O]\rightarrow C_2H_6+H_2O\,.$$

The participation of oxygen (in the given instance of the oxygen from the oxide, which plays the role of a solid oxidant) is an essential condition for the elimination of thermodynamic limitations to the formation of the C–C bond from the CH_4 molecules.[19]

The results of the above studies[16-19] stimulated research into the oxidative condensation of methane, which has led to the discovery of a direct pathway to the preparation from natural gas of a number of hydrocarbons and especially ethylene, whose synthesis had been based hitherto on the processing of petroleum raw material. The present review surveys and gives a systematic account of the results obtained in the selection of catalytic systems for the oxidative condensation of methane and analyses data concerning the conditions and mechanisms of the reactions leading to the formation of C_2 and other hydrocarbons from methane.

II. CATALYSTS OF THE OXIDATIVE CONDENSATION OF METHANE

The deliberate search for effective catalysts of the effective condensation of methane, which has been prosecuted simultaneously by many research groups in the USSR, Japan, the USA, and the Federal Republic of Germany, established the principal features of the catalytic reactions of methane in the presence of systems of different chemical composition. Among the catalysts investigated, three main classes, embracing oxide systems, oxide systems with alkaline additives, and catalysts containing halogen compounds, may be

distinguished. This classification reflects not only the greater complexity of the catalytic systems but also takes into account their greater effectiveness in the formation of C_2 and other hydrocarbons in the oxidation reactions of methane.

1. Oxide Systems

The results of a systematic study[19] of the oxidative condensation of methane in the presence of various oxides deposited on α-Al_2O_3 in amounts of 5–10 wt.% were published in 1982. The reaction was carried out in the presence of catalysts subjected to preliminary treatment with oxygen. The highest activity in the formation of C_2 hydrocarbons (ethane and ethylene) was shown by manganese, thallium, cadmium, and lead oxides (Table 1). Catalysts containing Zn, Ti, Zr, Mo, Fe, Cr, W, Cu, Ag, Pt, Ce, and V proved to be less active. According to the authors,[19] the reaction proceeds with participation of the oxygen from the oxide, as a result of which CH_3 species are formed on the surface of the catalyst, whose interaction leads to the formation of C_2H_6 molecules. Ethane can in its turn undergo oxidative dehydrogenation to ethylene. In order to regenerate the oxide after it has been in contact with methane, it must be treated with O_2-containing gas at the reaction temperature.

Table 1. The activities of certain metal oxides deposited on α-Al_2O_3 in the oxidative condensation of methane to ethane and ethylene at 800 °C[19]

Metal	Conversion of CH_4, %		
	w.r.t. C_2 hydrocarbons	CO_x	total
Initial carrier	0.2	1.6	1.8
Mn	5.0	6.0	11.0
Cd	4.0	6.0	10.0
Sn	0.4	8.0	8.4
Tl	3.0	3.8	6.8
Pb	2.0	2.6	4.6
Bi	0.4	4.0	4.4

The syntheses of C_2 hydrocarbons from methane under conditions where methane, an inert gas, and O_2 are supplied in succession have been proposed in patents.[20–30] Antimony, germanium, bismuth, lead, indium, and manganese oxides deposited on SiO_2 were used as catalysts, which functioned essentially as solid oxidants. At 700–800 °C the conversion of methane and the selectivity in the formation of C_2 hydrocarbons were 0.25–1.06 and 38.5–83.3% respectively. The successive introduction of the reactants into the catalytic zone evidently prevents the attainment of a satisfactory efficiency of the process, although the selectivity with respect to the C_2 hydrocarbons is relatively high.

Hinsen and Baerns,[31–34] investigated the possibility of the oxidative condensation of methane in the presence of O_2 on Pb-, Bi-, Sb-, Sn-, and Mn-containing catalysts. Among these systems, 34 wt.% PbO/γ-Al_2O_3 proved to be the most active catalyst. In its presence at 750 °C and for methane and O_2 contents in the reaction system of 50.9 and 5.2 vol.% respectively, the overall yield of C_2H_6 and C_2H_4 was about 5%. With increase in the PbO concentration in the catalyst, the selectivity in the formation of methane condensation products also increases (Fig.1), which has been attributed to the blocking of the acid centres on the carrier responsible for the extensive oxidation of the hydrocarbons.[34] The surface area of the catalyst also depends on the PbO content, diminishing from 166 $m^2\ g^{-1}$ (for the pure carrier) to 6 $m^2\ g^{-1}$ in the presence of 47 wt.% PbO/γ-Al_2O_3, which is evidently induced by the sintering of the catalyst at the reaction temperature. The influence of the nature of the carrier on the stability of the lead catalysts has been noted.[35] The use of aluminium and titanium oxides makes it possible to obtain systems whose catalytic properties do not change after use for 20–25 h; the lifetime of the SiO_2-based catalyst is significantly shorter, which is due to the loss of lead compounds and the sintering of the catalyst.

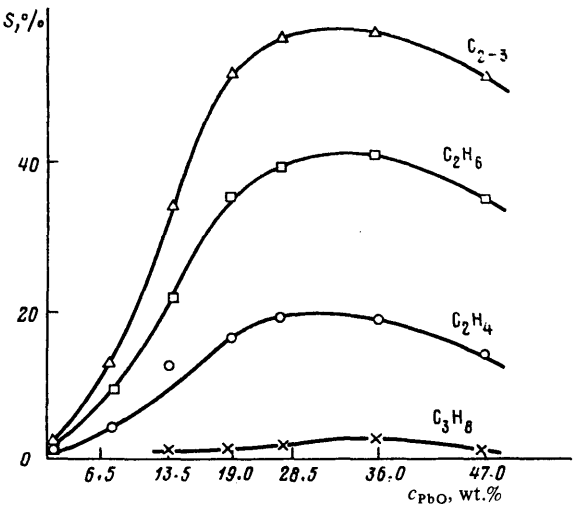


Figure 1. The selectivity S in the formation of the products of the oxidative condensation of methane in the presence of PbO/γ-Al_2O_3 with different contents c_{PbO} of PbO;[80] T = 740 °C; p_{CH_4} = 70.9 kPa; p_{O_2} = 7.1 kPa.

The increase in the process selectivity in the presence of lead systems is promoted by the increase in the reaction temperature and in the CH_4: O_2 ratio.[31] Together with C_2 hydrocarbons, the reaction products contain very small amounts of formaldehyde and propene; the extensive oxidation products were represented mainly by carbon dioxide. Only in the case of Sb_2O_3/SnO and Mn/Al_2O_3, which accelerated mainly the extensive oxidation process, did the selectivity in the formation of CO exceed 5%.[31]

Minachev et al. showed[36,37] that the efficiency of the manganese systems in the oxidative condensation of methane can be significantly increased by replacing the γ-Al_2O_3 carrier by silica gel. In the presence of Mn/SiO_2 containing the optimum amount of manganese in the form of the oxide (10 wt.%), at 750 °C and a volume flow rate v of the supply of the gaseous mixture of 1000 h^{-1}, and for the CH_4: air = 0.65 molar ratio, the conversion of CH_4 into C_2H_4 + C_2H_6 is 6.3%.[36] The possibility of the oxidative condensation of methane in the presence of Mn/SiO_2 has been confirmed.[38] Although PbO/γ-Al_2O_3 [31] and Mn/SiO_2 [36] have similar activities with respect to the overall yield of C_2 hydrocarbons, they differ appreciably as regards selectivity in the formation

of ethane and ethylene. The $C_2H_4 : C_2H_6$ molar ratio exceeds 1.3 for the manganese catalyst, while for the $PbO/\gamma\text{-}Al_2O_3$ catalyst it is in the range 0.23–0.95. Overall, the composition of the C_2 hydrocarbons formed depends, as will be shown below, not only on the nature of the catalyst but also on the reaction conditions.

The study of the catalytic properties of a large group of pure oxides at 700 °C, for the low $O_2 : CH_4 = 0.022$ molar ratio, and for a high dilution of the reaction mixture with helium (82%) established the following activity series: Sm > Pb > Bi > Ho > Gd > Fr > Tm, Yb, Y > La, Nd, Eu, Dy, Lu, Ca > Zn > Pr, Tb, Ce, Sc, Ge, In, Sn. Under these conditions, the lanthanide oxides exhibit a selectivity with respect to C_2 hydrocarbons greater than 75% and for the most active Sm_2O_3 the selectivity reaches 93%. It is noteworthy that in the presence of Sm_2O_3 the yield of C_2 hydrocarbons does not diminish even after the catalyst has been used for 180 h.[39] The appreciable activity of lanthanide oxides has been confirmed (for Sm_2O_3 and La_2O_3) by a number of data.[40–44] It has been observed that the efficiency of La_2O_3 increases after the addition of alumina[44] and increase in the fraction of the amorphous phase of the catalyst. According to Imai et al.,[44] the active centres for the oxidative condensation of methane are linked to aluminium ions dispersed in La_2O_3.

The ability of systems based on alkaline earth metals to accelerate the synthesis of C_2 hydrocarbons from methane has been demonstrated in a number of studies.[45–50] For the individual magnesium, calcium, strontium, and barium oxides, a steady increase in activity and selectivity with increase in the atomic weight of the metal is observed[45] (Table 2). On passing from MgO to BaO (750 °C), the yield of C_2H_4 and C_2H_6 increases from 4.4 to 15.2%, while the selectivity increases from 11.7 to 45.4%. It has been noted[45] that in the presence of SrO and BaO the reaction products contain no CO_2 during the first hours of the operation of the catalyst, which is associated with the conversion of the oxides into the carbonates. Comparison of the oxide and carbonate catalysts under identical conditions demonstrated the similarity of their properties in the oxidation (Table 2). The possibility of increasing both the activity and the selectivity of the catalyst by a preliminary heat treatment at 1000 °C (Table 2), which reduces the surface of the oxide by a factor of ~4, has been demonstrated for MgO.[48] The catalytic properties of alkaline earth metal oxides are also influenced by other factors, which is indicated by the increase in the activity of MgO after adding a small amount of barium compound (0.2 mole %) (Table 2), which is accompanied by the increase in the surface area of the catalyst from 70 to 200 $m^2\ g^{-1}$.[48]

Thus the oxidative conversion of methane into C_2 hydrocarbons can occur in the presence of a wide variety of oxide catalysts. It is difficult to differentiate any group of metals which is greatly superior in terms of activity and selectivity. Nevertheless, one may note that, with rare exceptions, there are no literature data concerning the use of oxide catalysts containing *d* transition metals, which exhibit a high activity for the extensive oxidation of hydrocarbons.[51,52]

Table 2. Catalytic properties of the catalysts of the oxidative condensation of methane containing alkaline earth metals.

Composition of catalyst	Reaction conditions			*B*, %	*S*, %	Refs.
	T, °C	Molar ratio of components	*v*			
MgO	800	$CH_4:O_2 = 5$	0.074 mol $g^{-1}\ s^{-1}$	5.2	50.0	[49]
	900	ditto	*	6.3	70	[47]
	700	$CH_4:O_2:He = 45.5:1:206.8$	—	—	38	[39]
	750	CH_4:air:He = 1:2.5:33.3	55.25 ml min^{-1}	4.4 **	11.7 **	[48]
	750	ditto	ditto	9.0 ***	26.1 ***	[48]
CaO	750	»	»	9.4	28.9	[45]
	800	»	»	12.8	39.1	[45]
	800	$CH_4:O_2 = 5$	0.074 mol $g^{-1}\ s^{-1}$	8.8	72.5	[49]
	700	$CH_4:O_2:He = 45.5:1:206.8$	—	****	70	[39]
SrO	750	CH_4:air:He = 1:2.5:33.3	55.25 ml min^{-1}	10.0	39.0	[45]
	800		ditto	16.3	52.7	[45]
$SrCO_3$	750	ditto	»	8.5	22.7	[45]
BaO	750	»	»	15.2	45.4	[45]
	800	»	»	16.6	44.6	[45]
	800	$CH_4:O_2 = 5$	0.074 mol $g^{-1}\ s^{-1}$	4.3	69.0	[49]
0.2 mole % Ca/MgO	750	CH_4:air:He = 1:2.5:33.3	55.25 ml min^{-1}	4	—	[48]
0.2 mole % Sr/MgO	750	ditto	ditto	4	—	[48]
0.2 mole % Ba/MgO	750	»	»	7.5	—	[48]
40 wt.% BaO/Al_2O_3	700	—	—	5	38	[50]
$BaCO_3$	800	CH_4:air:He = 7.6:1:29.4	64.6 ml min^{-1}	7.1	90.5	[45]
		CH_4:air:He = 1:2.5:33.3	55.25 ml min^{-1}	18.2	48.4	[45]

Notation: *B* is the yield of C_2 hydrocarbons and *S* the selectivity with respect to C_2 hydrocarbons.

* $\tau_{cont} = 0.5$ s.
** Heat treatment at 800 °C.
*** Heat treatment at 1000 °C.
**** Rate of formation 0.2 mol $min^{-1}\ m^{-3}$.

2. Oxide Systems with Added Alkali Metal Compounds

The modifying effect of added alkali metals on catalysts of different processes, including the partial oxidation of organic substances, is widely known.[53] The increase in the activity and selectivity of the catalyst by alkali metals is due to a number of causes, the main ones being the neutralisation of the acid centres of the carrier, the alteration of its adsorption characteristics, the weakening of the bonds between oxygen and the active components, and prevention of coke formation.[53]

The promoting effect of alkali metal additives on catalysts of the conversion of methane has been observed under conditions where methane and O_2 were supplied consecutively[54–79] and simultaneously.[80–98] For example, when methane came into contact with manganese systems modified by Li, Na, K, Rb, and Cs additives, the yield of the methane oxidative condensation products was higher than for the unpromoted solid carriers.[25,26] The conversion of methane, determined 2 min after the start of the experiment at 800 °C, was 7% in the presence of 10 wt.% Mn/SiO_2 with a selectivity in the formation of hydrocarbons of 55.6%. The addition of 1.7 wt.% Na (as the acetate) to the catalyst increases the conversion of methane and the process selectivity to 9 and 89.9% respectively. It has been noted[37,54] that the efficiency of the manganese systems investigated depends on the nature of the promoting additive and carrier and also on the method of their preparation.

The addition of Na (as sodium nitrite) to PbO/Al_2O_3 in an amount up to 4 wt.% increases the catalyst selectivity by ~10%, while the overall conversion of methane passes through a maximum when the Na_2O content in the catalyst is approximately 2 wt.%[80] (Fig.2). According to Hinsen et al.,[80] the

effect of Na is due to the neutralisation of the acid centres of the carrier, which, as already mentioned, promote the extensive oxidation of hydrocarbons. Accordingly, the promoting effect of added Na is manifested to a greater extent for catalysts prepared on the basis of acid carriers (γ-Al_2O_3, aluminosilicate).[80] The important role of the acid–base properties of the carrier is indicated by results[35] according to which the efficiency of the lead catalyst increases sharply when acid carriers are replaced by alkaline ones (CaO, SrO, BaO, and especially MgO).

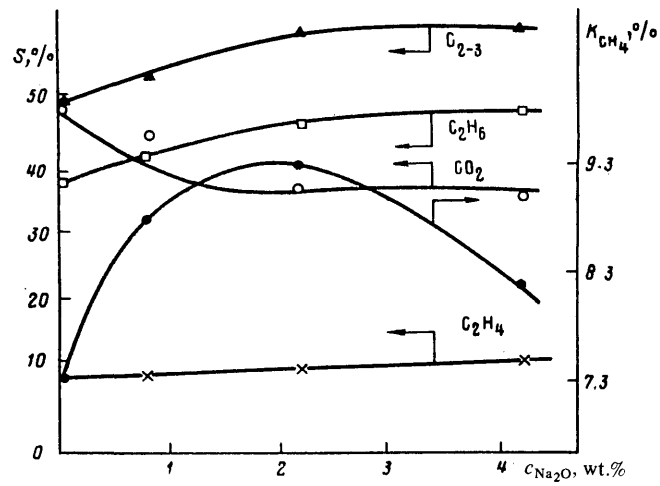


Figure 2. The influence of the alkaline additive on the catalytic properties of the 22 wt.% PbO/γ-Al_2O_3 catalyst in the oxidative condensation of methane;[80] T = 750 °C; p_{CH_4} = 70.9 kPa; p_{O_2} = 7.1 kPa; K_{CH_4} = conversion of methane.

Table 3. Oxidative condensation of methane in the presence of the 10 wt.% Mn/carrier catalyst[37] (T = 750 °C; molar ratio CH_4:air = 0.65; ν = 1000 h^{-1}).

Carrier	K_{CH_4}		S w.r.t. $C_2H_6 + C_2H_4$, %	Molar ratio C_2H_4:C_2H_6
	total	to $C_2H_6 + C_2H_4$		
γ-Al_2O_3	14.9	0.4	2.6	0.08
SiO_2	20.6	6.3	30.6	1.31
NaHSZ (X = 71)*	25.6	13.3	51.9	2.18
NaY (X = 4,4)	17.3	4.1	23.8	1.22
NaA (X = 2)	17.9	3.7	20.7	1.01

*$X = SiO_2/Al_2O_3$ (molar ratio).

The influence of alkaline components must be taken into account when materials such as zeolites, whose composition usually includes Na^+ cations, are used as carriers.[37] The higher efficiency of the Mn/NaHSZ zeolitic catalyst, compared with Mn/SiO_2, is probably associated with this factor (Table 3). The properties of zeolitic catalysts whose structures break up at the methane oxidative condensation temperature (700 to 800 °C) apparently depend also on the aluminium content in the zeolite. With decrease in the SiO_2/Al_2O_3 ratio in the carrier, i.e. with increase in the aluminium content, the yield of the C_2 hydrocarbons falls, although it still remains higher than in the presence of the γ-Al_2O_3-based catalyst (Table 3).

Systematic study of the effect of alkali metal additives on the Mn/SiO_2 catalysts[81] showed that the greatest promoting effect is exhibited by sodium (Table 4). At 800 °C and ν = 2000 h^{-1} in the presence of Mn/SiO_2 containing 4 wt.% Na, the yield of ethane and ethylene reaches 16.9% for a selectivity in the formation of C_2 hydrocarbons greater than 70%. The addition of lithium as the acetate to Mn/SiO_2 also increases the overall conversion of methane (to 25.4%), but the process becomes less selective owing to the increase in the yield of CO_2. Other alkali metals (K and Cs) increase the selectivity of the catalysts but lower their activity. The modification of Mn/SiO_2 by alkaline earth metal (Mg and Ca) compounds reduces appreciably the conversion of methane and the selectivity in the formation of C_2H_4 and C_2H_6 (Table 4). The effect of added alkali and alkaline earth metals on the properties of manganese catalysts[37,81] may be due to the decrease in the acidity of the catalytic systems and also to changes in the valence state of manganese and in the strength of the Mn–O bond.

Table 4. Catalytic properties of 10 wt.% Mn/SiO_2 with added 4 wt.% of alkali metal or alkaline earth metal (M) acetates in the oxidative condensation of methane[81] (T = 800 °C; molar ratio CH_4:air = 0.55; ν = 2000 h^{-1}).

M	K_{CH_4}, %	S, %		B, %	
		C_2H_4	C_2H_6	C_2 hydrocarbons	C_2H_4
—	16.4	41.3	7.3	8.0	6.8
Li	25.4	28.8	14.7	11.1	7.3
Na	23.9	67.5	3.0	16.9	16.1
K	11.3	49.9	13.5	7.2	5.6
Cs	11.2	39.0	14.4	6.0	4.4
Mg	11.5	16.0	11.6	3.2	1.8
Ca	13.5	13.4	10.5	3.3	1.8

The promoting effect of alkali metals has been observed for samarium,[82] zinc,[83] and bismuth oxides deposited on various carriers.[84] The characteristics of the variation of the catalytic properties of Sm_2O_3 and ZnO after the addition of alkali metal (Li, Na, K, Rb, and Cs) compounds are similar. The efficiency of the promoting additive decreases in both cases with increase in the atomic weight of the alkali metal.[82,83] In interpreting the effect of alkali metal additives, one should bear in mind that the promoting agent (Li), deposited on an inert carrier (SiO_2), is inactive in the conversion of methane (Fig. 3). The addition of 20 mole % of Li to Sm_2O_3 makes it possible to convert up to 21% of methane at 750 °C into C_2 hydrocarbons with a selectivity of 57%. This yield of C_2H_4 and C_2H_6 persists in the range of promoting agent concentrations from 10 to 30 mole %, while the maximum selectivity in the oxidative condensation of CH_4 is observed for 5–10 mole %.[82] According to Matsuura et al.,[83] an increase in the activity and selectivity of ZnO is observed when the fraction of Li in the catalyst is increased to 12.5 mole %; further growth of its concentration (up to 40 mole %) does not alter the catalytic properties of ZnO. The highest yield of C_2 hydrocarbons (23.9%) for a selectivity of 66.8% in the presence of Li/ZnO is obtained for a high dilution of the reaction mixture with helium (>80 vol.%) and for the molar ratio CH_4:O_2 = 2.[83]

Important results concerning the nature of the promoting effect of alkali metal additives have been obtained.[85,86] The $[Li^+O^-]$ centres containing active oxygen have been detected by EPR in MgO-based catalysts of the oxidative condensation of methane with added lithium carbonate. These centres are formed only at temperatures above 500 °C in an atmosphere of an O_2-containing gas. Their concentration increases significantly with increase in the partial pressure of O_2 to 13.3 kPa (Fig. 4). According to the authors,[85,86] the $[Li^+O^-]$ centres participate in abstracting H atoms from CH_4 with formation of methyl radicals:

$$[Li^+O^-] + CH_4 \rightarrow Li^+OH^- + CH_3^\cdot .$$

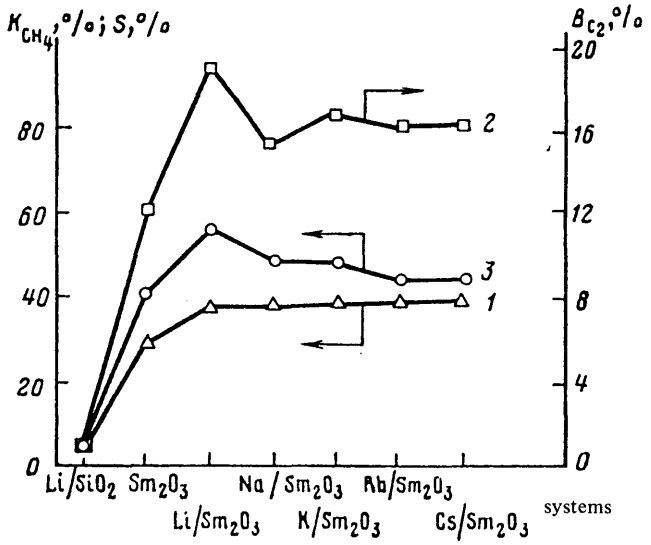


Figure 3. The effect of alkaline additives (20 mole %) on the conversion of methane (curve *1*), the yield *B* (curve *2*), and selectivity (curve *3*) in the formation of C_2 hydrocarbons in the presence of Sm_2O_3 catalysts of the oxidative condensation of methane;[82] T = 750 °C; p_{CH_4} = 5.1 kPa; p_{O_2} = 2.1 kPa; p_{He} = 94.1 kPa.

The $CH_3^\cdot$ radicals are intermediates in the reactions involving the partial and extensive oxidation of methane. The regeneration of the active centres of Li/MgO takes place after the dehydration of Li^+OH^- and the adsorption of O_2, accompanied by the dissociation of the O–O bond. Since these processes are endothermic, they take place at high temperatures.[86] Among the catalysts investigated, the 7 wt.% Li/MgO catalyst proved to be the most active. In its presence at 720 °C and for the molar ratios of the reaction mixture components $CH_4 : O_2 : He = 2 : 1 : 23$, the yield of C_2 hydrocarbons reached 19% for a selectivity of 50.3%. The Li/MgO system can serve as an example of the direct involvement of the promoting agent (the alkali metal) in the formation of active centres for the oxidative condensation of methane.

According to the data of Moriyama et al.,[87] added sodium nitrate has the greatest promoting effect on MgO, the effect of the nitrates of other alkali metals (Li, K, Rb, Cs) being less marked. In the presence of the catalyst with the optimum composition (15 mole % Na/MgO) at 800 °C and for the volume ratios CH_4 : air : He = 1 : 2.5 : 33.3, C_2 hydrocarbons are formed in 22.4% yield and with a selectivity of 56.8%. The increase in the Na content lowers significantly the thermal stability of the MgO crystal lattice: after heat treatment at 800 °C, the surface area of MgO is 70 $m^2\ g^{-1}$, while for the specimens with 15–20 mole % Na it is only 1–2 $m^2\ g^{-1}$. The authors[87] suggest that the reactions involving the generation of $CH_3^\cdot$ radicals, the extensive oxidation of the hydrocarbons, and the destruction of methyl radicals take place on the catalyst surface. A decrease in the area of the catalytic system retards the last two reactions to a greater extent, which increases the yield of the C_2 hydrocarbons and the process selectivity. The promoting effect of the alkali metal additive is apparently caused, together with other factors, by the modification of the carrier, which leads to the optimum morphology of the catalyst surface.

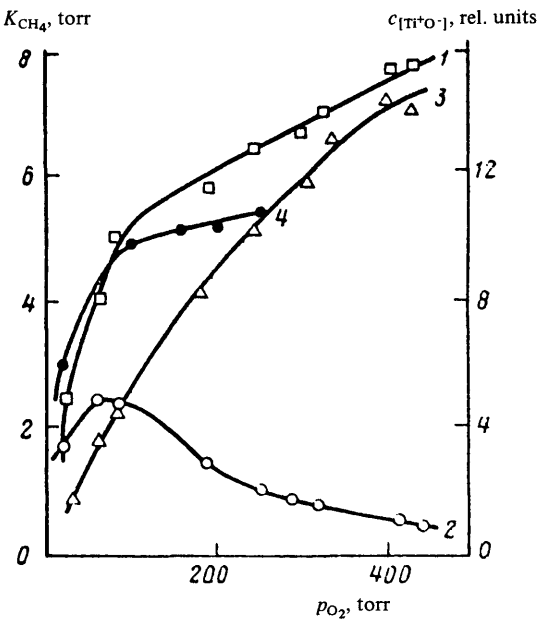


Figure 4. Dependence of the conversion of methane and of the concentration of the $[Li^+O^-]$ centres on the partial pressure of O_2:[86] 1) overall conversion of methane; 2) conversion into $C_2H_6 + C_2H_4$; 3) conversion into $CO + CO_2$; pCH_4 = 300 torr; T = 620 °C; catalyst—7 wt.% Li/MgO.

There are literature data[45,88,89] showing that the compounds of other alkaline earth metals (Ca, Sr, Ba) are also sensitive to alkali metal additives. Thus it has been shown that the catalytic properties of MgO and CaO modified with 5 mole % of Li, Na, K, or Cs[88] vary similarly: the yield of C_2H_4 and C_2H_6 and the selectivity in their formation decrease with increase in the ionic radius of the alkali metal (r_{M^+}). These relations have been explained taking into account the results of the X-ray diffraction analysis of the specimens heat-treated at 950 °C. If r_{M^+} is smaller than or equal to the radius of the alkaline earth metal (M^{2+}), then substitutional solutions with healing of the defects in the cationic sublattice are formed. On the other hand, when $r_{M^+} > r_{M^{2+}}$, then M^+ can enter the interstices, which increases the defectiveness

of the MO lattice as far as its conversion into the amorphous form. The latter promotes the adsorption of CO_2 and hence the blocking of the catalyst surface, which reduces its activity.[88] These considerations concerning the role of the conversion of the MO lattice into the amorphous form and the chemisorption of CO_2 in the deactivation of the catalyst differ from the hypotheses put forward by Aika et al.,[45] As already mentioned (Table 2), the formation of $BaCO_3$ from BaO under the conditions of oxidative condensation does not influence the yield of C_2 hydrocarbons, while the addition of Li, Na, K, or Rb compounds to $CaCO_3$ increases somewhat its activity but reduces its selectivity with respect to C_2H_4 and C_2H_6.[45]

On the basis of the data examined, one may conclude that the increase in the efficiency of the majority of catalysts of different nature as a result of the modification by alkali metal additives can be due to a number of causes. In acid systems, their effect is associated with the neutralisation of the acid centres accelerating the extensive oxidation of hydrocarbons. The interaction of alkali metal compounds with the catalysts at high temperatures (700–1000 °C) probably induces various changes in the crystal lattice and in the state of the catalytic surface. This usually leads to the conversion of the catalyst into an amorphous form and its sintering, which ensures the formation of the optimum surface of the catalytic system. Furthermore, alkali metal cations apparently promote the formation of centres containing active oxygen by creating defects and altering the effective charge on the ions localised on the catalyst surface.

Table 5. Catalytic properties of Sm_2O_3 modified by lithium compounds[99] (T = 750 °C; p_{CH_4} = 5 kPa; p_{O_2} = 2 kPa; p_{He} = 94 kPa).

Catalyst	K_{CH_4}, %		S, %	molar ratio $C_2H_4:C_2H_6$
	total	to $C_2H_4 + C_2H_6$		
Sm_2O_3	30.2	12.4	41.2	1.24
$LiBr/Sm_2O_3$	30.4	11.6	38.2	1.98
$LiCl/Sm_2O_3$	28.8	19.9	69.0	5.39
LiF/Sm_2O_3	26.5	13.9	52.6	1.00
$LiOH/Sm_2O_3$	38.2	19.5	51.1	1.09
$LiNO_3/Sm_2O_3$	37.5	19.5	51.9	1.17
Li_2CO_3/Sm_2O_3	41.2	22.3	54.1	0.95

3. Halogen-Containing Catalysts

The study of various catalytic systems promoted by alkali metal salts showed that their catalytic properties depend significantly on the nature of the anion of the added salt.[81,99–102] In the presence of Sm_2O_3,[99] the yield of the oxidative condensation products increases from 12.4% to 19.5–22.3 after the introduction of lithium chloride, hydroxide, nitrate, or carbonate (Table 5). The addition of LiBr and LiF hardly alters the conversion of methane into C_2 hydrocarbons. With the exception of the bromide, lithium compounds increase the selectivity in the formation of C_2H_4 and C_2H_6, the selectivity of $LiCl/Sm_2O_3$ being highest (69%). It is striking that the C_2 hydrocarbons formed in the presence of this catalyst consist mainly (to the extent of 84.4%) of ethylene. The fraction of ethylene in the presence of other catalysts is appreciably lower and is less than 50% for Li_2CO_3/Sm_2O_3. It has been suggested[99] that the observed effects are caused by the suppression of the extensive oxidation of the hydrocarbon by the added LiCl.

The fact that the addition of alkali metal salts to oxide catalysts having different chemical compositions induces similar changes in their activity and selectivity in the oxidative conversion of methane is important for the understanding of the nature of the catalytic action of the systems considered.[81,99,100] Indeed, as for samarium oxide modified by lithium compounds,[99,101] the efficiency of manganese catalysts[81] increases significantly after the introduction of sodium salts into their composition (Table 6). The nature of the halides influences also the proportions of the methane oxidative condensation products (Tables 5 and 6). For example, catalysts modified by LiF and NaF are inferior to other halogen-containing systems as regards selectivity in the formation of C_2H_4. Analogous behaviour has been observed[100] also for NiO + LiX (X = F, Cl, or Br). The addition of lithium and sodium chlorides induces the highest promoting effect; for $(Mn + NaCl)/SiO_2$, the yield of C_2 hydrocarbons reaches 25.8% for a selectivity in their formation of 77.5% (Table 6). The simultaneous increase in the activity and selectivity of the manganese catalyst cannot be explained solely by the suppression of the extensive oxidation of hydrocarbons, as suggested for $LiCl/Sm_2O_3$.[99,100] The Cl^- ions present in the catalyst are probably converted as a result of oxidation-reduction reactions into organochlorine compounds, which accelerate the formation of C_2H_4 and C_2H_6.

Table 6. The influence of the nature of the anion of the added sodium salt on the catalytic properties of Mn/SiO_2 in the oxidative condensation of methane[81] (T = 800°; molar ratio CH_4: air = 0.55; v = 2000 h^{-1}).

Salt	K_{CH_4}, %		S, %	Molar ratio $C_2H_4:C_2H_6$
	total	to $C_2H_4 + C_2H_6$		
—	16.4	8.0	48.6	5.7
CH_3COONa	23.9	16.9	70.5	20.1
NaF	22.3	9.8	43.9	2.9
NaCl	33.3	25.8	77.5	17.4
NaBr	26.8	19.2	71.6	26.4

The change in the catalytic properties of a number of transition metal oxides (Table 7) as a result of their modification by added LiCl has been investigated.[100,101] It must be emphasised that the individual oxides propagated only the extensive oxidation of methane under the selected conditions, while $LiCl/SiO_2$ did not exhibit an appreciable activity in the conversion of methane.[100] The combination of LiCl and metal oxides (with the exception of Fe and Cr) affords effective catalytic systems. Thus, in the presence of LiCl/Mn oxide, the conversion of methane into C_2 hydrocarbons is 30.6% for a selectivity of 64.7%. A high content of C_2H_4 in the methane oxidative condensation product is characteristic of all the catalysts (Table 7) and depends on the partial pressure of the reactants. In the case of LiCl/Mn oxide, the decrease of $p_{CH_4+O_2}$ from 85.5 to 7.65 kPa increases the fraction of C_2H_4 in the C_2 hydrocarbons from 67 to 92% with the simultaneous increase in the overall $C_2H_4 + C_2H_6$ yield by a factor of ~2.[100,101] The importance of the chloride component in the catalytic systems is also indicated by the decrease in the activity of LiCl/NiO with time, which is caused, according to the authors.[100,101] by the removal of LiCl from the catalytic zone. Patent data concerning the possibility of the activation by methylene chloride of the $NaMnO_2/MgO$

solid oxidant used in the cyclic conversion of methane agree with this finding.[103]

The efficiency of alkaline earth metal (Mg and Ca) oxides, in the presence of which the degree of conversion of methane into C_2H_4 and C_2H_6 at 800 °C is ~5%, increases after the addition of LiCl.[100] This is especially notable for the MgO systems: the yield and the selectivity in the formation of C_2 hydrocarbons increase from 4.8 to 19.4% and from 22.4 to 69.7% respectively, i.e. LiCl exhibits simultaneously a promoting effect and suppresses the extensive oxidation of methane. In the case of the oxides SiO_2 and Al_2O_3, which are inactive in the oxidative condensation of methane, the addition of LiCl increases the yield of C_2 hydrocarbons to only 3.6–3.7%.[100] The overall conversion of methane increases by a factor of ~2 (to 26.7%) on passing from Al_2O_3 to $LiCl/Al_2O_3$, mainly as a result of the formation of CO_2. This is the only example of the anomalous influence of LiCl on the catalytic properties of oxide systems in the oxidation reaction of methane.

Table 7. The influence of LiCl (20 mole %) on the catalytic properties of transition metal oxides[101] (T = 750 °C; p_{CH_4} = 5.1 kPa; p_{O_2} = 2.55 kPa; p_{He} = 93.7 kPa).

Metal	K, %		S, %	B, %	
	CH_4	O_2		$C_2H_4 + C_2H_6$	C_2H_4
Ti	17.6	40	82.8	14.6	13.6
Cr	26.1	85	0	0	0
Mn	47.3	95	64.7	30.6	28.1
Fe	22.2	92	0	0	0
Co	48.0	91	35.6	17.0	15.4
Ni	25.9	57	71.8	18.6	14.5
Cu	49.5	80	20.6	10.2	10.2
Zn	22.0	49	68.9	15.2	9.4

The above results[100,101] make it possible to compare the influence of the nature of alkali metals, whose chlorides have been used to modify nickel, samarium, and europium oxides. In the presence of nickel catalysts with 20 mole % MCl (M = Li, Na, or Cs), the yield of C_2 hydrocarbons decreases from 18.6% (Table 7) to 6.2% and to 5.9% with increase in the atomic weight of M. The fraction of C_2H_4 in the methane condensation product diminishes at the same time from 78.0 to 58.0 and to 42.4%, although a parallel variation of the selectivity in the series of these catalysts is not observed. Systems based on Eu_2O_3 and containing LiCl and NaCl hardly differ as regards the yield of C_2H_4 and C_2H_6 but the selectivity of the catalyst with added NaCl is somewhat higher than for the specimen promoted with LiCl. Among the Sm_2O_3 catalysts modified with sodium, potassium, and caesium chlorides, the Na and Cs systems proved to be the most active. The KCl/Sm_2O_3 catalyst exhibits a higher selectivity with respect to C_2 hydrocarbons while being inferior to other Sm_2O_3 systems in terms of the overall conversion of methane (by a factor of ~2). These data show that lithium and sodium chlorides have the greatest promoting effect, although the nature of the carrier also plays a significant role in this case.

Bivalent and tervalent metals [metal halides] deposited on pumices, kieselguhr, and titanium, zinc, magnesium, and calcium oxides can be used as the active components of the halides in the preparation of halogen-containing catalysts of the oxidative condensation of methane.[102] At 750 °C and for the volume ratio CH_4:air = 2:1, $BaBr_2$, $MgCl_2$, $CaCl_2$–$MgCl_2$, $CaCl_2$–LiCl–$CeCl_3$, and $CaCl_2$–LiCl–$PrCl_3$ deposited on pumice exhibit a high efficiency. The yield of the methane condensation products in the presence of these systems is in the range 13–15% for a selectivity of 80–90%. Catalysts which consist of melts of individual salts or mixtures with alkali metal halides (LiCl, CsCl, KBr, and KI) on carriers show a lower activity under the same conditions. The high concentration of C_3 and C_4 hydrocarbons in the methane condensation products obtained in the presence of a series of catalysts with bivalent metal halides is striking. Thus the fraction of butenes is 46.8 and 24.1% respectively in the presence of $BaBr_2$/pumice and $CaBr_2/MgO$. The selectivity of the systems considered with respect to C_3 and C_4 hydrocarbons depends on the nature of the salts and carriers used. For catalysts obtained by depositing $BaBr_2$ on pumice, CaO, ZnO, and silicon carbide, the content of C_3 and C_4 hydrocarbons in the methane condensation products is reduced from 46.8 to 33.9%, which indicates the possibility of regulating the degree of the oxidative condensation of methane by varying the composition of the catalyst.

Thus the efficiency of halogen-containing catalysts in the oxidative condensation is greater than that of other catalytic systems. The promoting function of the halide components is due to a number of factors. Their involvement in the formation of intermediates in the oxidative condensation of methane and in the suppression of processes involving the extensive oxidation of hydrocarbons appears to be extremely probable. The latter factor is indicated, in particular, by the results of studies of the deactivation by the chloro- and bromo-derivatives of methane and ethane of palladium and platinum catalysts of the extensive oxidation of methane.[104] These chloro- and bromo-derivatives are adsorbed preferentially on the centres responsible for the activation of oxygen reacting with methane. Additional evidence in support of the concept of the inhibition of the extensive oxidation of hydrocarbons is provided by data indicating a sharp change in the selectivity of the oxides of a series of transition metals in the oxidation reaction of methane after the addition of halide salts, which leads to the preferential formation of the products of the oxidative condensation of methane. On the other hand, these systems are more effective than non-transition metal halides deposited on inert carriers, which indicates the interaction of the halide component with transition metal compounds under the catalytic conditions. Such interaction apparently induces the formation of active halogen species promoting the condensation of methane. This agrees with the decrease in the activity of the catalysts as a result of the loss of the halide component and the possibility of an increase in their activity following the addition of volatile halogen compounds to the reaction mixture. A high content of ethylene in the C_2 hydrocarbon formed is characteristic of the catalysts considered, i.e. the presence of halogens influences different stages of the catalytic process, including the stages responsible for the appearance of different proportions of the methane condensation products.

III. THE MECHANISM OF THE OXIDATION REACTIONS OF METHANE

Comparison of the properties of catalysts of different classes makes it possible to discover a series of common features of the oxidative condensation of methane. The most important factor is that C_2 hydrocarbons are formed in the presence of all the catalysts only at temperatures above 550–600 °C. Fig. 5 presents typical temperature variation of the yield of the products of the extensive and partial

oxidation of methane in the presence of a manganese catalyst.[37] Up to 600 °C, the only products are carbon oxides and water and under these conditions the oxygen in the gas mixture is almost fully converted (to an extent greater than 95%). At higher temperatures, the formation of C_2H_6 and C_2H_4 is observed, their yield increasing up to 800 °C. At the same time there is an increase in the selectivity with respect to the C_2 hydrocarbons and the oxidative condensation of methane becomes the dominant process at temperatures above 750 °C. It is noteworthy that, in the presence of Mn/NaHSZ at 700–800 °C, ethylene is formed in greater amounts than ethane, which may be associated with the increase in the rate of dehydrogenation of ethane on passing to high temperature.

The character of the oxidative conversion of methane is determined, apart from reaction temperature, by the contact time and the ratio of the components of the reaction mixture.[37,80,83,105] The kinetic relations (Fig. 7*a*) obtained for low conversions of O_2 on Sm_2O_3 [105] show that the selectivity with respect to C_2 hydrocarbons increases steadily with decrease in p_{O_2} and approaches 100% for $p_{O_2} < 0.3$ kPa. The increase in the selectivity in the oxidative condensation of methane and in the rate of formation of the methane conversion products is favoured by an increase in p_{CH_4} (or in the ratio $CH_4:O_2$), which is clearly manifested in the range of p_{CH_4} from 0 to 30 kPa (Fig. 7*b*).

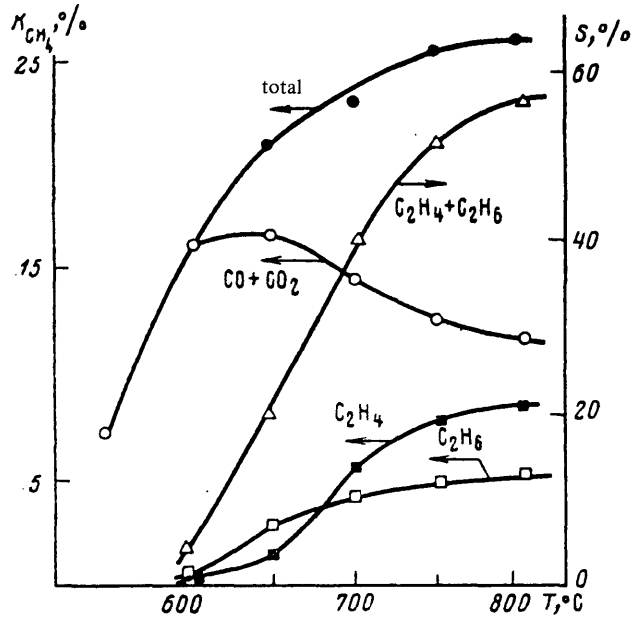


Figure 5. The influence of temperature on the yield of the products of the oxidation reactions of methane:[81] 10 wt.% Mn/NaHSZ (X = 71); molar ratio CH_4:air = 2:3; ν = 1000 h^{-1}.

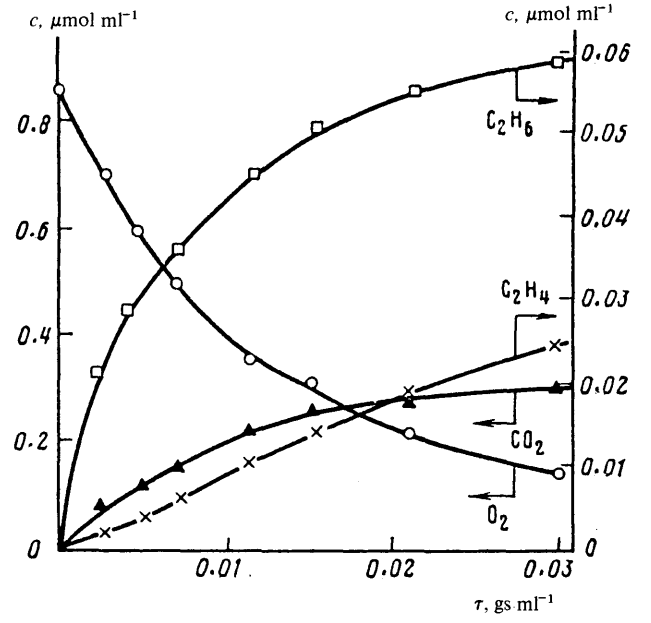
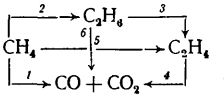


Figure 6. Dependence of the yield of the products of the oxidative condensation of methane on the contact time τ on $PbO/\gamma\text{-}Al_2O_3$;[80] T = 700 °C; c_{CH_4} = 5.0 mol ml^{-1}; p_{CH_4} = 40 kPa.

It has been shown for the $PbO/\gamma\text{-}Al_2O_3$ [80] and Li/MgO [86] catalysts that an increase in the contact time τ leads to an increase in the yield of the products of the extensive and selective oxidation of methane. In the presenece of the lead system (Fig. 6), the yield of ethylene varies linearly over the entire range of values of τ and the conversion of CH_4 into C_2H_6 after long contact times tends to a limit. This increases the ratio C_2H_4/C_2H_6, indicating the consecutive formation of C_2H_4 from C_2H_6. It has been noted for Li/MgO [86] that the curves for the formation of the methane oxidation products at 620 °C do not pass through the origin of coordinates. Since diffusion-dependent obstacles are unlikely on Li/MgO in view of the low surface area of the catalyst (2 m^2 g^{-1}) and the absence of micropores, the authors[86] attribute the observed variation to the possibility of the reaction of methane via a chain mechanism.

The composition of the products formed as a result of the extensive oxidation and the oxidative condensation of methane suggests a mechanism reflecting the following possible reactions of the hydrocarbons:



The contribution of the individual reactions to the overall processes can be inferred from data obtained in studies[86,105] of the reactions of individual hydrocarbons under the conditions of the oxidative condensation of methane. The results of experiments on the oxidation of CH_4, C_2H_6, and C_2H_4 in the presence of Sm_2O_3 are presented in Table 8. The initial C_2H_6 and C_2H_4 partial pressures correspond to the pressures of these substances in the mixture obtained on oxidation of methane. Evidently the main bulk of CO and CO_2 is formed as a result of the direct oxidation of methane (see Scheme

above, reaction 1), which is consistent with data for Li/MgO, in the presence of which the yield of CO and CO_2 in the oxidation of methane is greater by a factor of 3.6 than in the oxidation of ethane. The fact that the CO and CO_2 partial pressures are somewhat smaller in the oxidation of C_2H_4 (Table 8) than in the oxidation of C_2H_6 indicates a greater involvement of ethane in the extensive oxidation reaction (reaction 5) than that of ethylene (reaction 4).

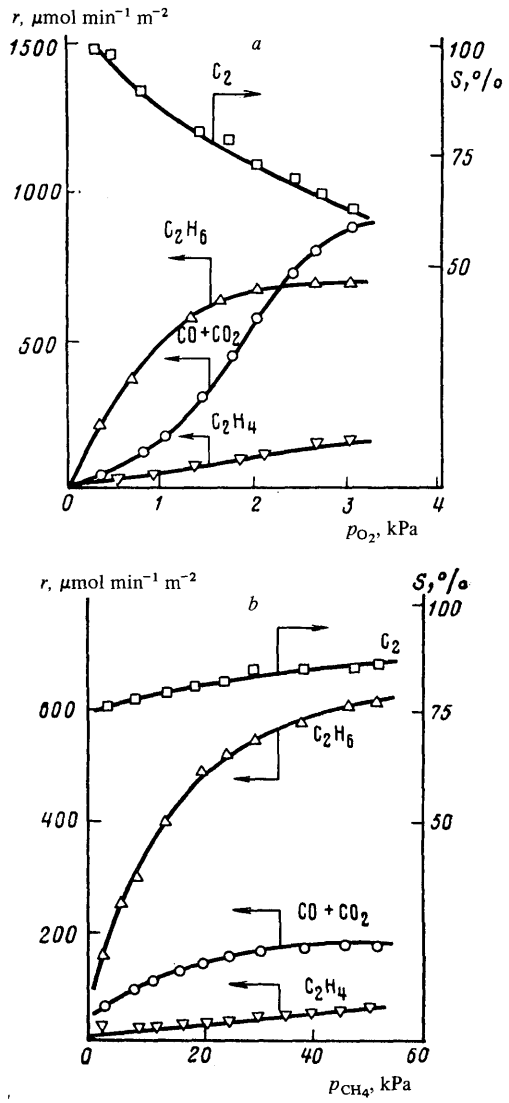


Figure 7. The influence of the partial pressures of O_2 (*a*) and CH_4 (*b*) on the rate of formation of the products of the oxidative conversion of CH_4 (*r*) and on the selectivity with respect to C_2 hydrocarbons;[105] catalyst—Sm_2O_3; T = 700 °C; p_{CH_4} = 18.2 kPa; p_{O_2} = 0.98 kPa.

Comparison of the rates of formation of C_2H_4 from CH_4 and C_2H_6 (Table 8) shows that they differ little, i.e. that C_2H_4 is formed from ethane—the primary product of the oxidative condensation of methane, and not via reaction 6 (see Scheme).

Table 8. The partial pressures of the methane oxidation products over Sm_2O_3 [105] (T = 710 °C; mass of Sm_2O_3 = 3.3 mg; v = 37.5 ml min^{-1}).

Initial hydrocarbon	Partial pressures of compounds, kPa					
	O_2	CH_4	C_2H_6	C_2H_4	CO_2	CO
CH_4	$9.2\cdot10^{-1}$	7.7	$1.2\cdot10^{-2}$	$1.6\cdot10^{-4}$	$1.1\cdot10^{-2}$	$0.2\cdot10^{-3}$
C_2H_6	$9.2\cdot10^{-1}$	0	$1.3\cdot10^{-2}$	$2.0\cdot10^{-4}$	$9.5\cdot10^{-4}$	$2.4\cdot10^{-4}$
C_2H_4	$9.2\cdot10^{-1}$	0	0	$2.0\cdot10^{-6}$	$6.4\cdot10^{-6}$	0

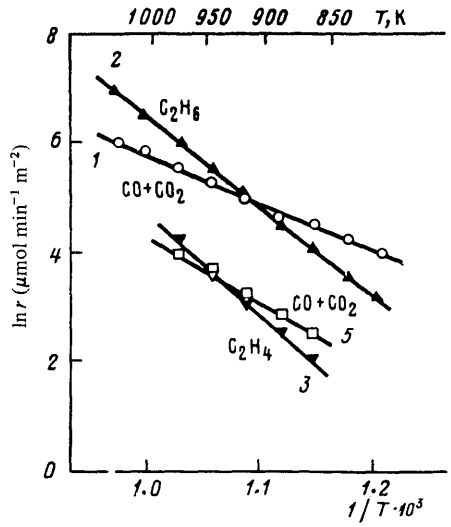


Figure 8. The Arrhenius relations for the extensive and selective oxidation reactions of CH_4 (lines *1* and *2*) and C_2H_6 (lines *3* and *5*) in the presence of Sm_2O_3 [105] (the numerals correspond to the numbers of the reactions presented in the Scheme); p_{CH_4} = 18.2 kPa; p_{O_2} = 0.98 kPa.

The apparent activation energies E_{act} calculated from the data in Fig. 8 [105] for the extensive oxidation of CH_4 and C_2H_6, the oxidative condensation of CH_4 to C_2H_6, and the oxidative dehydrogenation of C_2H_6 to C_2H_4 in the presence of Sm_2O_3 are respectively 66, 94, 135, and 173 kJ mol^{-1}. The higher values of E_{act} for the formation of C_2H_6 and C_2H_4 compared with E_{act} for the extensive oxidation of hydrocarbons show that an increase in temperature promotes the selective conversion of methane into C_2 hydrocarbons. An important factor is that such differences have been discovered for a whole series of catalysts containing lead,[80] barium, cadmium, tin, antimony, and thallium[89,106] oxides. Under comparable conditions, the E_{act} for the selective conversion of methane are within a narrow range of values for catalysts of different chemical nature. Consequently, the mechanism of the formation of C_2 hydrocarbons can include stages characteristic of a wide range of catalytic systems, for example, the formation of CH_3 radicals on the surface of the catalyst and their transfer to the gas phase.[86] The heterogeneous-homogeneous mechanism is supported by the similarity of the E_{act} for the formation of C_2 hydrocarbons and methyl radicals,[89,106] whose existence has been confirmed by EPR.[47,107]

The important role of the $CH_3^{\bullet}$ species in the oxidative conversion of methane is indicated by data for isotope exchange between CD_4 and CH_4 in the presence of oxide catalysts.[84,108] It was found that only one hydrogen atom exchanges in the adsorption–desorption cycle of the CH_4 molecule, which has been explained by the dissociative reaction of CH_4 on the surface of the oxide with formation of the $CH_3^{\bullet}$ and $H^{\bullet}$ species. The removal of hydrogen is facilitated by the formation of C_2H_6 from the $CH_3^{\bullet}$ radicals, so that the active catalyst should combine, according to the authors,[84] the functions ensuring the dissociation of CH_4 and the oxidation of $H^{\bullet}$.

Nowadays the majority of investigators believe that the active centres of the oxide catalysts on which the $CH_3^{\bullet}$ species are generated contain oxygen in one state or another.[86,105,109,114] Thus the formation of $CH_3^{\bullet}$ radicals is regarded[109] as a result of the interaction of CH_4 with the oxygen in the crystal lattices of the oxides. This conclusion is based on the fact that the amount of oxygen incorporated in the reaction product after CH_4 has been in contact with the solid oxidant exceeds the amount of oxygen in the surface layer by a factor of 10–20, i.e. the oxygen present in the bulk of the oxide enters into the reaction. Under the catalytic conditions, the main bulk of the $CH_3^{\bullet}$ radicals are probably formed with participation of the oxygen in the surface layer of the oxide, whose loss is made good by the O_2 from the gas phase. As already mentioned, the active centres in Li/MgO [86] are regenerated by the reaction of O_2 with the structural defects in MgO. This induces the appearance of the coordination-unsaturated O^- species, whose concentration is correlated with the content of Li^+ in the catalyst and with the rate of formation of the $CH_3^{\bullet}$ radicals (Fig. 4).

Another state of active oxygen has been detected on La_2O_3 after its treatment in an atmosphere of an O_2-containing gas at 650 °C and rapid cooling to −196 °C.[43] The EPR spectra of the oxide contained lines whose g-factors ($g_{\parallel} = 2.047$, $g_{\perp} = 1.994$) are characteristic of the superoxide ion O_2^-. The conclusion that diatomic oxygen species (O_2, O_2^-, or O_2^{2-}) participate in the dissociation of the C–H bond in the CH_4 molecule was reached[111,112] on the basis of kinetic studies of the oxidative condensation of CH_4 in the presence of Sm_2O_3. This agrees with the finding that the peroxides Na_2O_2, SrO_2, and BaO_2 are capable of oxidising methane to C_2 hydrocarbons at relatively low temperatures (200–450 °C).[113,114] The interaction of methane with the peroxide oxygen in Na_2O_2 involves the surface and deep layers of the Na_2O_2 lattice, which is indicated by the ratio of the oxygen in the reaction products and in the outer layer of the oxidant.[113] Comparison of the apparent E_{act} for the oxidative condensation of methane (59 kJ mol^{-1}) and decomposition of BaO_2 (142–192 kJ mol^{-1}) indicate the involvement of the peroxide ions O_2^{2-} in the reaction and not of the gaseous O_2 formed on thermal dissociation of BaO_2 [89,114] Thus the state of the active oxygen can be influenced by the nature of the promoting agent and the oxide employed. At the same time, for a number of catalysts, for example, those which contain chlorides, one cannot rule out the generation of the $CH_3^{\bullet}$ radicals when methane interacts with the halide components of the reaction system.[81,100]

The question of the site where the methyl radicals recombine has been confirmed in a number of investigations.[16,19,86,106] It has been suggested[19] that ethane is formed as a result of the dimerisation of the $CH_3^{\bullet}$ species on the surface of the solid oxidant with subsequent dehydrogenation of the adsorbed C_2H_6 to C_2H_4. Another view has been expressed[109] on the basis of kinetic data obtained in the cyclic oxidation of methane in the presence of Mn/SiO_2 (Fig. 9). Extrapolation of the relations presented shows that the selectivity in the formation of all the products (with the exception of ethane) tends to zero with decrease in contact time. The increase in the selectivity with respect to C_2H_6 under the given conditions has been explained[109] by the gas-phase interaction of the $CH_3^{\bullet}$ radicals, because strong adsorption of these species on the Mn/SiO_2 surface should also lead to the formation of C_2H_4 and the extensive oxidation products.

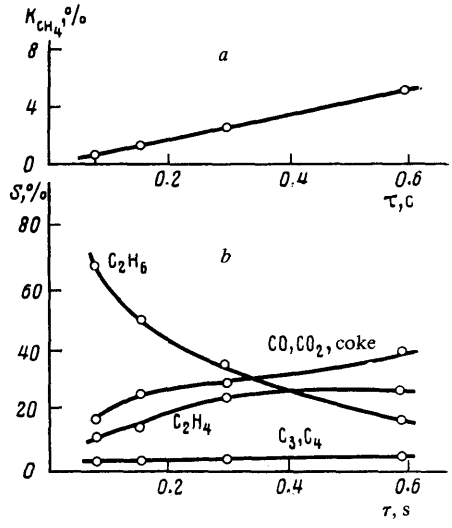


Figure 9. Dependence of the degree of conversion of methane and of the selectivity in the conversion process on the time of contact with the solid oxidant 5 wt.% Mn/SiO_2 at 800 °C [109] (data obtained 1 min after the start of the experiment).

The conclusion that the gas-phase dimerisation of the $CH_3^{\bullet}$ radicals takes place has also been reached by other investigators[86,106] who studied the catalytic conversion of methane in the presence of gaseous oxygen. According to the mechanism proposed,[86] after their appearance on the surface, the $CH_3^{\bullet}$ radicals pass to the gas phase, where they form C_2H_6. The methyl species can also interact with oxygen, affording the methylperoxy-radicals $CH_3O_2^{\bullet}$, which are intermediates in the extensive oxidation reaction. This agrees with the increased yield of CO and CO_2 following an increase in the partial pressure of O_2 [37,83,105] and also with the finding that the main bulk of carbon oxides are formed from methane under the conditions of the oxidative condensation of methane and not from C_2H_6 or C_2H_4 [86,105] (Table 8). It is noteworthy that the $CH_3O_2^{\bullet}$ species are fairly stable up to ~500 °C, as has been established in the gas-phase oxidation of methane by oxygen.[116] The decrease in the O_2 concentration and the increase in temperature therefore promote the decomposition of $CH_3O_2^{\bullet}$ into O_2 and $CH_3^{\bullet}$, which leads ultimately to an increase in the selectivity with respect to C_2 hydrocarbons.[43] The gas-phase oxidation is probably not the only pathway to the formation of CO and CO_2 under the conditions of the catalytic conversion of methane. The heterogeneous occurrence of the extensive oxidation process is indicated by the large amount of carbon oxides formed in the reaction of CH_4 with the solid oxidant in the presence of gaseous oxygen.[109] Lunsford and co-workers[86] assumed that extensive oxidation includes the interaction of the $CH_3^{\bullet}$ radicals with the O^{2-} ions

of the catalyst. Unfortunately there are insufficient data to infer the nature of the surface intermediates and the centres responsible for their extensive oxidation.

Together with the generation of the $CH_3^{\cdot}$ radicals and the formation of carbon oxides, the oxidative dehydrogenation of ethane can be attributed to reactions occurring on the surfaces of the catalysts. This is indicated indirectly by numerous data (see Section II) for the dependence of the C_2H_4/C_2H_6 ratio on the composition of catalysts used under identical conditions. In particular, the introduction of dehydrogenating additives (ZnO, NiO) into PbO/Al_2O_3 increases the fraction of ethylene in the products of the oxidative condensation of methane.[115] It has been suggested[89] that, when PbO/Al_2O_3 is used, ethane is formed from methane and ethylene is formed from ethane (in contrast to the extensive oxidation reaction) on the same active centres. According to Ito et al.,[86] the first stage in the dehydrogenation of C_2H_6 in the presence of Li/MgO takes place with participation of O^- ions and the $C_2H_5^{\cdot}$ radicals formed in this process are converted into C_2H_4 under the influence of the O^{2-} anion in the oxide lattice. As shown in the previous Section, the fraction of ethylene in the C_2 hydrocarbons formed in the presence of halogen-containing catalysts is much greater than in the presence of oxide systems. It has been suggested[100] that the dehydrogenation of C_2H_6 is accelerated in the gas phase by the $Cl^{\cdot}$ radicals, although this has not so far been confirmed directly.

Data indicating the formation of hydrocarbons containing three and more carbon atoms together with C_2H_6 and C_2H_4 are of undoubted interest both from the standpoint of the elucidation of the nature of the reactions occurring in the oxidative condensation of methane and from the practical point of view. C_3 and C_4 hydrocarbons are most frequently detected when the methane conversion is carried out under cyclic conditions.[109] Kinetic investigations have shown[109] that the increase in the duration of contact between methane and the solid Mn/SiO_2 oxidant increases the content of ethylene, propene, and butenes and reduces the fraction of ethane in the methane condensation products (Fig.9), which indicates the successive formation of C_2–C_4 olefins from C_2H_6. Furthermore, the yield of C_3H_6 and C_4H_8 increases appreciably when ethylene and propene are added respectively to methane. Hence it follows that the degree of the oxidative condensation of methane is controlled by the intensity of the reactions between the olefins formed and the $CH_3^{\cdot}$ radicals.[109] The absence of appreciable amounts of C_3 and C_4 hydrocarbons under the catalytic conditions may be associated with the high concentration of oxygen in the gas phase and on the catalyst surface, which promotes the extensive oxidation of these hydrocarbons and the intermediates involved in their formation. It may be expected that further study of the mechanism of the oxidative reactions in the CH_4–O_2–catalyst system will yield new results elucidating further the synthetic possibilities of the oxidative condensation of methane.

The solution of the problem of the activation of methane and of its selective conversion into valuable products is of fundamental and practical importance. The steadily increasing stream of information about the direct synthesis of C_2 and other hydrocarbons from methane shows that, in essence, a new field has been established in the chemistry of methane. There is no doubt that the practical application of the oxidative condensation of methane still requires the solution of a number of complex theoretical and applied problems. The improvement of the catalytic conversion of methane is associated in the first place with a deeper understanding of the reaction mechanism, of the nature of the active centres in the catalytic systems, and of their deactivation processes. However, considerable advances have already been made in the development of effective catalysts and in the selection of optimum conditions for the oxidative condensation of methane.

In the presence of the most active and selective catalysts, methane can be converted to the extent of 40% in a single pass with a selectivity of 70–80% with respect to C_2 hydrocarbons.[81,116] It is important that such results have been obtained for mixtures with high concentrations of the starting materials and at high volume flow rates. In many cases the C_2 hydrocarbons contain up to 95 vol.% of ethylene, which is of exceptional interest in connection with the steadily growing requirements for this product, whose world production will reach ~45 million tonnes according to predictions for 1990.[117]

The preparation of ethylene from natural gas will reduce the consumption of the petroleum raw material in this industry. Furthermore, the ethylene formed by the oxidative conversion of methane, can be almost fully converted, without being isolated from the gaseous mixture, into other olefins and aromatic hydrocarbons[118] in the presence of zeolites of the pentasil type.[7] Thus the oxidative condensation of methane opens a pathway to the synthesis of various compounds which are currently obtained by the processing of petroleum. The role of such processes will probably increase greatly in the future, because any depletion in the available resources of methane can be made good by the biochemical decomposition of a wide variety of organic substances.

REFERENCES

1. V.G.Fastovskii, "Metan" (Methane), Gos.Nauch.-Tekh.Izd.Neftyanoi i Gorno-Toplivnoi Lit., 1947.
2. D.R.Stull, E.F.Westrum, and G.C.Sinke, "The Chemical Thermodynamics of Organic Compounds" (Translated into Russian), Izd.Mir, Moscow, 1971, p.186.
3. N.N.Lebedev, "Khimiya i Tekhnologiya Osnovnogo Organicheskogo i Neftekhimicheskogo Sinteza" (The Chemistry and Technology of Fundamental Organic and Petrochemical Synthesis), Izd.Khimiya, Moscow, 1981.
4. A.E.Shilov and G.D.Shul'pin, Priroda, 1985(8), 128.
5. E.A.Grigoryan, Uspekhi Khim., 1984, **53**, 348 [Russ. Chem.Rev., 1984(2)].
6. R.Pitchai and K.Klier, Catal.Rev.Sci.and Eng., 1986, **28**, 13.
7. Kh.M.Minachev and D.A.Kondrat'ev, Uspekhi Khim., 1983, **52**, 1921 [Russ.Chem.Rev., 1983(12)].
8. J.R.Anderson and P.Tsai, Appl.Catal., 1985, **19**, 141.
9. K.G.Ione, V.G.Stepanov, V.N.Romannikov, and S.S.Shepelev, Khim.Tverd.Topliva, 1982(6), 35.
10. V.N.Romannikov and K.G.Ione, Kinetika i Kataliz, 1984, **25**, 92.
11. S.S.Shepelev and K.G.Ione, Kinetika i Kataliz, 1984, **25**, 347.
12. Europ.P.93453; Chem.Abs., 1984, **100**, 71054.
13. Kh.E.Khcheyan, O.M.Revenko, A.V.Borisoglebskaya, and Yu.Z.Fradkov, Neftekhimiya, 1981, **21**, 83.
14. Kh.E.Khcheyan, A.N.Shatalova, O.N.Temkin, and O.M.Revenko, Neftekhimiya, 1981, **21**, 303.
15. Kh.E.Khcheyan, G.L.Bitman, L.V.Rashchupkina et al., USSR P.1074854; Byul.Izobret., 1984(7), 86.
16. US P.417810; Chem.Abs., 1980, **92**, 146938.
17. US P.4205194; Chem.Abs., 1981, **94**, 106257.
18. US P.4239658; Chem.Abs., 1981, **94**, 106257.

19. G.E.Keller and M.M.Bhasin, J.Catal., 1982, **73**, 9.
20. US P.4443644; Chem.Abs., 1984, 101, 9892.
21. US P.4443645; Chem.Abs., 1984, **101**, 9891.
22. US P.4443646; Chem.Abs., 1984, **101**, 195008.
23. US P.4443647; Chem.Abs., 1984, **101**, 9890.
24. US P.4443648; Chem.Abs., 1984, 101, 9889.
25. US P.4443649; Chem.Abs., 1984, 101, 9888.
26. B.P.2156842.
27. US P.4523060.
28. US P.4554395; Chem.Abs., 1986, **104**, 209157.
29. US P.4560821; Chem.Abs., 1986, 104, 188706.
30. B.P.1398385. Chem.Abs., 1976, **84**, 7402.
31. V.W.Hinsen and M.Baerns, Chem.-Ztg., 1983, **107**, 223.
32. BRD P.3237079.
33. US P.4608449; Chem.Abs., 1986, **104**, 7497.
34. M.Baerns, Nachr.Chem., Techn.Lab., 1985, **33**, 292.
35. K.Asami, S.Hashimoto, T.Shikada, et al., Chem.Lett., 1986, 1233.
36. Kh.M.Minachev, N.Ya.Usachev, Yu.S.Khodakov, et al., Izv.Akad.Nauk SSSR, Ser.Khim., 1985, 1686.
37. Kh.M.Minachev, N.Ya.Usachev, Yu.S.Khodakov, et al., Izv.Akad.Nauk SSSR, Ser.Khim., 1987, **504**.
38. I.A.Guliev, Sh.A.Nuriev, S.A.Dzhamalova et al., Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 11.05.86, No.3393-V.
39. K.Otsuka, K.Jinno, and A.Morikawa, Chem.Lett., 1985, 499.
40. Japanese P.6138627; Chem.Abs., 1986, **105**, 103447.
41. Europ.P.189079; Chem.Abs., 1986, **105**, 135942.
42. H.Imai and T.Tagawa, J.Chem.Soc.Chem.Comm., 1986, 52.
43. C.H.Lin, K.D.Campbell, J.-X.Wang, and J.H.Lunsford, J.Phys.Chem., 1986, **90**, 534.
44. H.Imai, T.Tagawa, and N.Kamide, "VIII Japan–USSR Catalytical Seminar. Catalysis by New Materials", Tokyo, 1986, p.139.
45. K.Aika, T.Moriyama, N.Takasaki, and E.Iwamatsu, J.Chem.Soc.Chem.Comm., 1986, 1210.
46. A.I.Suleimanov, S.V.Aliev, and V.D.Sokolovskii, Article Deposited at the All-Union Institute of Scientific and Technical Information (VINITI), 11.10.85, No.7220-V.
47. D.E.Driscoll, W.Martir, J.-X.Wang, and L.H.Lunsford, J.Amer.Chem.Soc., 1985, **107**, 58.
48. E.Iwamatsu, T.Moriyama, N.Takasaki, and K.Aika, J.Chem.Soc.Amer.Comm., 1987, 19.
49. E.Yamagata, K.Tanaka, S.Sasaki, and S.Okazaki, Chem.Lett., 1987, 81.
50. M.Ya.Sinev, V.N.Korchak, and O.V.Krylov, "Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Mekhanizmu Kataliticheskikh Reaktsii" (Abstracts of Reports at the IVth All-Union Conference on the Mechanisms of Catalytic Reactions), Moscow, 1986, Part 2, p.27.
51. L.Ya.Margolis and O.V.Krylov, "Glubokoe Kataliticheskoe Okislenie Uglevodorodov (Problemy Kinetiki i Kataliza. T.18)" [The Extensive Catalytic Oxidation of Hydrocarbons (Problems of Kinetics and Catalysis, Vol.18)], Izd.Nauka, Moscow, 1981, p.120.
52. B.M.Kadenatsy and M.D.Shibanova, "Glubokoe Kataliticheskoe Okislenie Uglevodorodov (Problemy Kinetiki i Kataliza. T.18)" [The Extensive Catalytic Oxidation of Hydrocarbons (Problems of Kinetics and Catalysis, Vol.18)], Izd.Nauka, Moscow, 1981, p.124.
53. W.D.Mross, Catal.Rev.Sci.and Eng., 1983, **25**, 591.
54. C.A.Jones, J.J.Leonard, and J.A.Sofranko, J.Catal., 1987, **103**, 311.
55. US P.4450310.
56. US P.4489215.
57. US P.4499322; Chem.Abs., 1986, **104**, 209957.
58. US P.4499323; Chem.Abs., 1985, **102**, 151958.
59. US P.4499324.
60. US P.4495374; Chem.Abs., 1985, **102**, 116407.
61. US P.4517398.
62. US P.4547608; Chem.Abs., 1986, **104**, 71534.
63. US P.4544785.
64. US P.4544786.
65. US P.4544787.
66. US P.4547607; Chem.Abs., 1986, **104**, 209947.
67. US P.4547610; Chem.Abs., 1986, **104**, 71535.
68. US P.4547611.
69. US P.4544395.
70. US P.4556749; Chem.Abs., 1986, **104**, 53400.
71. US P.4567307; Chem.Abs., 1986, **105**, 155993.
72. B.P.2148935; Chem.Abs., 1985, **103**, 144646.
73. Europ.P.147327; Chem.Abs., 1986, **105**, 26143.
74. International P.00804; Chem.Abs., 1985, **103**, 8825.
75. International P.04821; Chem.Abs., 1986, **104**, 71539.
76. International P.04866; Chem.Abs., 1986, **104**, 91876.
77. International P.04867; Chem.Abs., 1986, **104**, 71538.
78. International P.04054; Chem.Abs., 1986, **105**, 229642.
79. E.Y.Garsia, G.L.Rivera, D.E.Resasco, React.Kinet. and Catal.Lett., 1985, **28**, 431.
80. W.Hinsen, W.Bytyn, and M.Baerns, "Proceedings of VIII International Congress on Catalysis", West Berlin, 1984, 3, 581.
81. Kh.M.Minachev, N.Ya.Usachev, V.N.Udut, et al., Izv.Akad.Nauk SSSR, Ser.Khim., 1987, 2124.
82. K.Otsuka, Q.Lin, M.Hatano, and A.Morikawa, Chem. Lett., 1986, 467.
83. I.Matsuura, Y.Utsumi, M.Nakai, and T.Doi, Chem. Lett., 1986, 1981.
84. I.T.Emish and I.Amenomiya, J.Phys.Chem., 1986, **90**, 4785.
85. T.Ito and J.H.Lunsford, Nature, 1985, **314**, 721.
86. T.Ito, J.-H.Wang, C.-H.Lin, and J.H.Lunsford, J.Amer.Chem.Soc., 1985, **107**, 5062.
87. T.Moriyama, N.Takasaki, E.Ewamatsu, and K.Aika, Chem.Lett., 1986, 1165.
88. M.Yu.Sinev, P.A.Shiryaev, V.N.Korchak, and O.V.Krylov, "Doklady V Neftekhimicheskogo Simpoziuma Sotsialisticheskikh Stran" (Reports at the Vth Petrochemical Symposium of Socialist Countries), Burgas, Bulgaria, 1986, p.101.
89. M.Yu.Sinev, Candidate's Thesis in Chemical Sciences, Institute of Chemical Physics, USSR Academy of Sciences, Moscow, 1987.
90. Europ.P.198251; Chem.Abs., 1986, **105**, 229636.
91. US P.4620057; Chem.Abs., 1987, **106**, 52112.
92. BRD P.3508571; Chem.Abs., 1987, **106**, 5592.
93. BRD P.3406751; Chem.Abs., 1986, **104**, 7497.
94. US P.4523049; Chem.Abs., 1985, **103**, 87486.
95. J.A.Roos, A.G.Bakker, H.Bosch, et al., Catal., Today, 1987, 1, 133.
96. C.A.Jones, J.J.Leonard, and J.A.Sofranko, Energy Fuels, 1986, **1**, 12.
97. W.R.Patterson, Appl.Catal., 1986, **24**, 329.
98. J.Ross, Appl.Catal., 1986, **23**, 218.
99. K.Otsuka, Q.Lin, M.Hatano, and A.Morikawa, J.Chem.Soc.Chem.Comm., 1986, 586.
100. K.Otsuka, M.Hatano, Q.Lin, and A.Morikawa, "VIII Japan–USSR Catalytical Seminar. Catalysis by New Materials", Tokyo, 1986, p.1.

101. K.Otsuka, Q.Lin, M.Hatano, and A.Morikawa, Chem. Lett., 1986, 903.
102. BRD P.3503664; Chem.Abs., 1986, **105**, 153683.
103. US P.4544784.
104. C.F.Gullis and B.M.Willatt, J.Catal., 1984, **86**, 187.
105. K.Otsuka, K.Jinno, and A.Morikawa, J.Catal., 1986, **100**, 353.
106. M.Yu.Sinev, G.A.Vorob'eva, and V.N.Korchak, Kinetika i Kataliz, 1986, **27**, 1164.
107. D.J.Driscoll and J.H.Lunsford, J.Phys.Chem., 1985, **89**, 4415.
108. L.J.Quanzhi and Y.Amenomiya, Appl.Catal., 1986, **23**, 173.
109. J.A.Sofranko, J.J.Leonard, and C.A.Jones, J.Catal., 1987, **103**, 302.
110. K.Otsuka, S.Yokoyama, and A.Morikawa, Chem. Lett., 1985, 319.
111. K.Otsuka, Q.Lin, and A.Morikawa, Inorg.Chim.Acta, 1986, **23**, 118.
112. K.Otsuka and X.Jinno, Inorg.Chim.Acta, 1986, **121**, 237.
113. K.Otsuka, A.A.Said, K.Jinno, and T.Komatsu, Chem.Lett., 1987, 77.
114. M.Yu.Sinev, V.N.Korchak, and O.V.Krylov, Kinetika i Kataliz, 1986, **27**, 1274.
115. A.V.Nalbandyan, and I.A.Vardanyan, "Sovremennoe Sostoyanie Problemy Gazofaznogo Okisleniya Organicheskikh Soedinenii" (The Present State of the Problem of the Gas-Phase Oxidation of Organic Compounds), Izd.Akad.Nauk Arm.SSR, Erevan, 1986, p.195.
116. K.Otsuka and T.Komatsu, J.Chem.Soc.Chem.Comm., 1987, 388.
117. Information Chimie, 1984, **249**, 123.
118. K.Otsuka and T.Komatsu, Chem.Lett., 1986, 1955.

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