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Oxidative Processing of Light Alkanes: State-of-the-Art and Prospects

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Abstract—Recent literature data on partial oxidation of light alkanes into syngas and oxidative coupling of methane into C_2 hydrocarbons are reviewed. The problems of these processes (high cost of pure oxygen; safety; activity, selectivity and stability of catalysts; temperature regime; coke formation and other by-products; insufficient level of methane transformation into ethane and ethylene) are considered. Possible solutions of these problems and prospects of practical use of light alkanes processing are discussed.

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INTRODUCTION

The chemistry of light alkanes is one of the most vigorously developing branches of science [1–8]. This fist of all is due to increasing demand for natural and gases as source materials for chemical industry because of the inevitable reduction of объемов petroleum production. The other reason is that these highly stable hydrocarbons are quite difficult to activate. Thermodynamic restrictions can be overcome by means of oxidation of hydrocarbons with oxygen or compounds containing active oxygen. However, a new problem therewith arises, associated with deep oxidation and reduced selectivity with respect to target products. This problem can be solved by optimizing partial oxidation conditions and using highly active, selective, and stable catalysts.

The present review presents the most important findings in the field of oxidative processing of light alkanes into syngas and direct reforming of methane into C_2 hydrocarbons, thus characterizing the present state of problem and prospects of its further development.

Oxidative Reforming of C_1–C_4 Hydrocarbons into Syngas

General Information

Synthesis gas or syngas (a mixture of CO and H_2) is produced by steam methane reforming (SMR):

$$CH_4 + H_2O \rightarrow CO + 3H_2\ (\Delta H^0 = 206\ \text{kJ mol}^{-1}), \qquad (1)$$

carbon dioxide methane reforming (CDMR):

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2\ (\Delta H^0 = 247\ \text{kJ mol}^{-1}), \qquad (2)$$

and partial methane oxidation (PMO):

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2\ (\Delta H^0 = -36\ \text{kJ mol}^{-1}). \qquad (3)$$

The first two reactions are highly endothermic, and PMO involves slight heat release.

In industry syngas is commonly manufactured by steam reforming of natural gas. This technology features two essential drawbacks: high hydrogen content of syngas, which makes the latter difficult to use, say, for example, for the synthesis of hydrocarbons and methanol, and high energy consumption. These circumstances encourage development of new catalysts and processes combining SMC and methane oxidation with oxygen. The advantages of combined technologies consist in the compensation of the heat effects of reactions (1) and (3), as well as that allow manufacturing syngas with the CO/H_2 ratio close to 2.

The three SMC technologies of methane reforming into syngas are similar in that they are all high-temperature processes (800°C and higher) and occur in the presence of Group VIII metals in close-to-equilibrium conditions. Until now there has been no reliable information in the literature that the oxidation of methane with oxygen at low temperatures can result in preferential formation of CO and H_2.

It should be noted that real temperatures of processes with a large heat effect are quite difficult to measure. Thus Gladky et al. [9] studied the oxidation of propane into syngas on a nickel tape by means of thermography and mass spectrometry *in situ* to show that the rate of propane oxidation oscillates as the catalyst temperature periodically varies. Further difficulties in measuring the heat effect arise when metals on low-conductivity supports are used as catalysts. Heat release in hydrocarbon oxidation can not only result in a considerable overheat of active components of catalyst (by 100°C and more). The temperature measured with a thermocouple placed in the catalyst layer is not always correct. This circumstance prompted a series of works in 1992–1993 on low-temperature (450–500°C) synthesis of syngas from methane at high volume rates (cf. [5], p. 35). Actually, the catalyst temperature measured with an infrared thermometer was very high (1200–1300°C). The aforesaid should be borne in mind in considering the results of other authors who mention PMO at relatively low temperatures [10].

Group VIII metals (except for iron whose oxides are hardly reducible) are the most active catalysts of all methane reforming processes. These metals are extremely active in the decomposition of methane into carbon and hydrogen. Abundant evidence is presently available showing that C–H bond cleavage in the key stages in all the three syngas production processes [5, 6, 8]. At present two mechanisms of PMO are considered:

(1) consecutive mechanism, specifically deep oxidation of methane into CO_2 and H_2O with catalyst oxygen (lattice or adsorbed) at the first stage

$$CH_4 + 4O_{cat} = CO_2 + 2H_2O \quad (4)$$

and subsequent steam or carbon dioxide reforming of methane along reactions (1) and (2);

(2) direct mechanism, specifically complete dissociation of methane and oxygen on the surface:

$$CH_4 = (\text{via the sequence } CH_4 \rightarrow CH_3 \rightarrow CH_2 \rightarrow CH \rightarrow C) = C + 4H_{ads}, \quad (5)$$

$$O_2 = 2O_{ads} \quad (6)$$

and reaction between adsorbed species:

$$C + O_{ads} = CO, \quad (7)$$

$$2H_{ads} = H_2. \quad (8)$$

At present experimental evidence is available for both the consecutive and direct mechanisms of CO and H_2 formation, and one can mention a number of factors affecting the mechanism of PMO. They include the nature and state of the catalyst (dispersity of the metal, its oxidation degree, and nature of metal-carbon, metal-oxygen, metal-hydrogen, and metal-support interactions), as well as reaction conditions (CH_4/O_2 ratio, partial pressure of the components of the reaction mixture, actual temperature profile of the catalyst layer, etc.).

The great variety of these factors and the possibility that the reaction medium can affect the state of the catalyst makes it difficult to draw a clear border between the PMO mechanisms. When the consecutive mechanism is operative, the question of whether CH_4 molecules react with reduced metal centers arises. For a “pure” consecutive mechanism we can admit that they are very fast oxidized with gaseous oxygen, to exclude the stage of methane dissociation, which takes place in the direct mechanism. On the other hand, the direct PMO should be accompanied by steam or carbon dioxide methane reforming because of the inevitable formation of H_2O and CO_2. It is quite probable that PMO involves a number of reactions that occur concurrently in the heterogeneous system $(CH_4 + O_2)$–catalyst–$(CO + H_2 + H_2O + CO_2 + C)$.

Problems of the Partial Oxidation of Hydrocarbons into Syngas and Ways to Their Solution

Partial oxidation of hydrocarbons is normally performed using pure oxygen rather than air to avoid dilution of syngas with nitrogen. However, separation of air requires a considerable energy consumption that comprises 40% of the cost of syngas [8]. One more serous disadvantage of PMO consists in that $CH_4 + O_2$ mixtures are explosive. A radical solution of these problems could be provided by performing PMO in a reactor with walls made of oxygen-conducting membranes.

Large-scale R&D into such membranes was undertaken in the USA at the end of the past century by leading chemical companies and the Argonne National Laboratory. In particular, Sr–Fe–Co–O mixed oxides possessing electronic and ionic conductivities were shown to hold promise [11, 12]. A membrane tubular reactor was manufactured by plastic extrusion and tested at 900°C for 1000 h. Methane was fed into the reactor, and, due to the high oxygen permeability of the reactor walls, CH_4 reforming attained 98% at a 90% selectivity with respect to CO. Other effective membrane materials for air separation have been reported [6, 8]. It has recently been shown that the mobility of lattice oxygen and membrane efficiency can be much enhanced in nanostructured mixed oxides of cerium and other rare-earth metals, doped with platinum and palladium [13].

Membrane reactors for PMO have certain serious drawbacks preventing their commercialization. They include the mechanical strength of the membranes, which decreases at a very high gradient of O^{2-} concentration at membrane boundaries one of which is in contact with air and the other resides in a reductive medium. Membrane reactors can be destroyed when hermetically connected to metal parts of an apparatus, since the expansion coefficients of metals and ceramics strongly differ from each other.

One more way to approach the problems associated with air separation and explosiveness of $CH_4 + O_2$ mixtures is to oxidize methane with the lattice oxygen of metal oxides. Therewith, the catalyst functions as oxygen carrier and works in a cyclic regime: After syngas has been produced, the reduced catalyst is oxidized with air [reactions (9) and (10) for nickel oxide as example). Thus, no pure oxygen is required to produce the $CO + H_2$ mixture, and the process safety is enhanced.

$$CH_4 + NiO = CO + 2H_2 + Ni, \tag{9}$$

$$Ni + 0.5O_2(air) = NiO. \tag{10}$$

The total heat effect of reactions (9) and (10) will be equal to the quantity of heat released by PMO (36 kJ mol^{-1}).

As catalysts for two-stage PMO a variety of oxides containing transition metals (Ni, Cu, Fe, REM, Cr, etc.) was suggested [6, 8]. A $La_{0.8}Sr_{0.2}Co_{0.5}Fe_{0.5}O_{3-\delta}$ perovskite was found to be highly active in PMO, but the process was complicated by deep methane oxidation and coke formation [14]. Much attention is paid to cerium oxides [15–19]. Individual CeO_2 [15] is capable of oxidizing methane already at 600°C, and the reaction products contain H_2 and CO in a 2:1 ratio. Modifying CeO_2 with Gd and Nd oxides favors reduced coke formation by decreasing the oxidation temperature [16]. Wei et al. [17] showed that the methane reforming on a 10% $CeO_2/\gamma\text{-}Al_2O_3$ catalyst at 870°C attains 61% at high selectivities with respect to both H_2 and CO (89 and 91%, respectively).

Introduction of noble metals into cerium-containing systems exerts a considerable effect on the activity of the latter in methane oxidation in the absence of gaseous oxygen. Jalibert et [18] found out how the yield of CO and H_2 depends on the degree of reduction of $Pt/CeO_2/\gamma\text{-}Al_2O_3$, which can be controlled by duration of redox cycles. Platinum and ruthenium catalysts applied on the mixed oxide $Ce_{1-x}Zr_xO_2$ (x = 0, 0.2, 0.5) were studied in the temperature range 550–700°C [19]. Platinum catalysts proved to be more active than ruthenium ones. The presence of ZrO_2 in the support favors faster methane oxidation, but, therewith, the selectivity of CO and H_2 is reduced. The prevailing process observed on oxidized catalysts was deep CH_4 oxidation, and after partial oxidation of the samples the selectivity in CO and H_2 increased up to 90%. This result suggests that the reactivity of lattice oxygen changes with its removal from the oxide system. Note that ZrO_2 and $ZrO_2–Y_2O_3$ containing no noble metal additives contain 8 and 14 mol % of oxygen capable of reacting with methane at 900°C [20].

Quite important is the problem of catalyst deactivation. This relates not only to PMO, but also to steam and carbon dioxide reforming. The loss of catalytic activity is most frequently associated with the cocking of active components and catalyst carbonizetion. The carbon that forms represents nanotubes whose growth blocks active centers and destroys catalyst granules. Carbonization can be prevented by increasing the fraction of oxidant in the mixture (O_2, H_2O, or CO_2) but in this case the composition of syngas may change in an undesirable way.

Another approach to the problem is to develop stable and effective catalysts. The catalyst activity is higher, if the rate of oxidation of carbon is higher than the rate of its formation.

The properties of a catalytic system are much dependent on the way the system has been prepared. In the following section we consider the recent literature data just from this viewpoint.

Catalysts for Partial Hydrocarbon Oxidation into Syngas

Most attention in the development of catalysts has been paid to systems containing Ni [21–28], Rh [10, 29–32], Pt [29, 33, 34], Pd [35], and Ru [31]. As shown in [22], Ce included in the composition of Ni catalysts $Ce_{1-x}Ni_xO_y$ (x = 0.05–0.6) enhances their efficiency and stability. The strongest effect was attained at x = 0.4, when the selectivity in H_2 and CO was 80 and 90%, respectively; therewith, the catalyst could work for 160 h with no activity loss. Based on the data of X-ray phase analysis, temperature-programmed reduction, and X-ray photoelectron spectroscopy for fresh and spent catalysts, Shan et al. [22] suggested that the oxidative reforming of methane involves the Ce^{+3}/Ce^{+4} and Ni^{+2}/Ni^0 ion pairs. An important role in carbon oxidation also belongs to lattice oxygen activated by Ce^{+3} cations.

We observed enhanced activity of metals on cerium oxide supports in various oxidation reactions [36]. The activity enhancement is associated with a high mobility of oxygen in the CeO_2 lattice, and this activity increases in going to mixed oxides, in particular to Ce–Zr–O [37, 38]. Comparison of the properties of Pt/CeO_2, Pt/ZrO_2, and $Pt/Ce_xZr_{1-x}O_2$ in PMO [33, 34] revealed the highest activity of $Pt/Ce_xZr_{1-x}O_2$. Its ability to donate oxygen ensures fast oxidation of carbon deposits.

An important factor controlling the catalytic activity is dispersity of Group VIII metals. Solid solutions NiO–MgO [27] supported by metal foams are active in PMO at a high volume rate of the $2CH_4+O_2$ gas mixture (up to 19 l g^{-1} h^{-1}). The rate of carbon accumulation on solid supports is much lower than in the presence of powdered NiO–MgO oxides in the absence of a support. The nature of active component–support interaction could be affected by modifying the latter [39]. The 6% Co/Al_2O_3 catalyst was found to be poorly active in PMO and underwent rapid deactivation, but its activity was enhanced by doping CaO, and methane reforming was no longer accompanied by carbon formation. Gao et al. [39] explained the observed effects by that CaO favors Co_3O_4 reduction under the reaction conditions, thereby decreasing the size of metallic cobalt and slowing down $CoAl_2O_4$ formation. Stabilization of high-dispersity Co^0 and Ru^0 particles by the matrix of reduced $LaFe_{1-x}Co_xO_3$ [40] and $La_{1-x}Ca_xRu_{1-x}Ni_xO_3$ perovskites [41] which exhibit a high stability in PMO has been reported.

The promising techniques for the preparation of catalysts are solid-phase crystallization, sol–gel procedure, etc. [11]. The method of support (ZrO_2) preparation affects the activity and stability of Ni catalysts [42]. Three samples were synthesized by three different procedures: hydrothermal, drying and calcinating alcogel in nitrogen, and traditional precipitation. The first two procedures gave oxide particles uniform in shape (spherical and rod-like). Nickel applied on them was in a high-dispersity state, which prevented carbonization of the Ni/ZrO_2 catalyst during PMO. By preparing the Ni/La_2O_3 catalyst by the sol–gel procedure, Liu et al. [43] could obtain nanosized Ni^0 particles, unlike what could be obtained by traditional wet impregnation [43].

Specific Features of Partial Oxidation of Methane Homologs into Syngas

The interest in processing ethane, propane, or other light alkanes into syngas is associated with the fact that these hydrocarbons are present in natural and oil gases whose separation into individual components is inexpedient by one or another reason. In selecting catalysts and optimizing conditions for joint reforming of light hydrocarbons of extreme importance is the question of catalyst stability, since in going to methane homologs the probability of alkane cracking and catalyst carbonization increases.

Group VIII metals are also applied in the partial oxidation of C_2 and C_3 hydrocarbons [21, 44–73]. At the same time, other catalytic systems, in particular those on the basis of vanadium pentoxide, are known [74]. Ma et al. [69] determined the relative reactivities of methane, ethane, and propane in partial oxidation. A mixture of these hydrocarbons with oxygen (alkane/O_2 = 0.9) was passed through a layer of the Pt/Al_2O_3 catalyst which was heated at a rate of 10°C/min. It was found that the oxidation initiation temperatures of CH_4, C_2H_6, and C_3H_8 were 368, 242, and 178°C, i.e. the reactivity increases in parallel with the molecular weight of the hydrocarbon. Corbo and Migliardini [21] performed a comparative study of the partial oxidation of methane and propane on two catalysts containing nickel and platinum. As seen from Table 1, the propane conversion of 88–95% is attained at temperatures 70–100°C lower than a 60–75% methane conversion.

The problem of carbonization of promoted NiO/γ-Al_2O_3 catalysts in the course of ethane reforming was considered by Liu et al. [71]. Additions of Li and La favor a much lower carbonization rate: At 850°C within 5 h, the carbon deposition was 2.5%, and on the modified catalyst at the same conditions it decreased to 0.4%. Promoting Ni–Mg hydrotalcite with ruthenium decreased the carbon deposition on the partial oxidation of propane at 700°C over the course of 7.5 h from 40 to 6 wt % [62].

Alkane reforming is affected if there is water vapor in the reaction mixture. Pino et al. [58] observed stable work of the Pt/CeO_2 catalyst in the combined oxidative and steam propane reforming (complete conversion of propane at 650°C and volume rate 25000 h^{-1}). No

Table 1. Partial oxidation of methane and propane [21]. $V = 620\ \mathrm{l\ h^{-1}\ g_{kg}^{-1}}$, $O_2/C = 0.53$

Alkane	Catalyst	t, °C	Conversion of alkane, %	Yield of H_2,%	Yield of $CO+CO_2$, %	$S(H_2)$, %
CH_4	$14\%NiO/13\%Ca/Al_2O_3$	900	75	64	75	85
	$1\%Pt/CeO_2$	870	60	44	60	75
C_3H_8	$14\%NiO/13\%Ca/Al_2O_3$	~800	95	88	92	95
	$1\%Pt/CeO_2$	~800	88	58	72	75

carbon deposition was observed even after 100 h. The same effect of water vapor was observed in the autothermal oxidative reforming of propane in the presence of Ni/Al_2O_3 [55].

The problem to reduce carbon deposition gets even more complicated, if the starting mixture contains C_{1+} hydrocarbons. Liu et al. [52] have studied the possibility of producing syngas from CH_4–C_2H_6–CO_2–O_2 and CH_4–C_2H_6–C_3H_8–C_4H_{10}–CO_2–O_2 mixtures on the LiLaNiO/γ-Al_2O_3 catalyst. No appreciable carbon deposition was observed in the case of the methane–ethane mixture. Propane–butane mixtures were found to be very difficult to process because of carbon deposition of reactor walls. In the latter case, a two-stage scheme was suggested, involving initial oxidation of C_3H_8 and C_4H_{10} to CO_2 at a temperature below 600°C, followed by reforming the CH_4–C_2H_6–CO_2–O_2 mixture on LiLaNiO/γ-Al_2O_3 at higher temperatures.

The above examples show that the problem of catalyst carbonization is much complicated with complicating composition of the raw material for syngas production. This problem can be approached via systematic research on the development of stable catalysts and optimization conditions for the partial oxidation of mixtures of C_1–C_4 hydrocarbons into syngas.

Direct Methane Reforming to C_2 Hydrocarbons

Commercial methane processing into valuable products (higher hydrocarbons, oxygen-containing compounds) involves cleavage of all C–H bonds in CH_4 followed by their formation (Fischer-Tropsh synthesis, oxosynthesis, etc.). Since the early 1980s, there has been intensive search for catalysts for direct methane reforming to C_{2+} hydrocarbons, catalytic properties of diverse materials in oxidative methane coupling (OMC) have been studied. In particular, highly efficient Mn-containing catalysts for OMC have been developed at the Institute of Organic Chemistry of the Russian Academy of Sciences (IOC RAS) [1–4].

Mechanism of Oxidative Methane Coupling

There is abundant published evidence [5, 6] in favor of the heterogeneous–homogeneous nature of the oxidative methane coupling in the presence of catalysts. Methane molecules are activated on catalyst oxygen centers, resulting in hydrogen abstraction and $CH_3^{\cdot}$ formation:

$$CH_4 + O_{cat} \rightarrow CH_3^{\cdot} + H\text{–}O_{cat}.$$

The necessary condition for OMC to occur is that $CH_3^{\cdot}$ radicals pass into the gas phase, which prevents their oxidation on catalyst surface. In the gas phase $CH_3^{\cdot}$ radicals undergo dimerization to form ethane:

$$2CH_3^{\cdot} \rightarrow C_2H_6.$$

Catalyst regeneration involves oxidation of surface O–H groups with oxygen:

$$2H\text{–}O_{cat} + 0.5O_2 \rightarrow 2O_{cat} + H_2O + H^{\cdot}.$$

Under OMC conditions, ethylene is formed by thermal or oxidative dehydrogenation of ethane. The role of oxidant can be played by catalyst (O_{cat}) or gas-phase (O_2) oxygen.

Among catalysts for OMC, no systems active in deep hydrocarbon oxidation have been suggested (except for modified rare-earth metal and manganese oxides). The catalysts combine basicity and a moderate oxidative ability, which is associated with the necessity of a fairly fast desorption of $CH_3^{\cdot}$ radicals into the gas phase. There properties are responsible for the high OMC temperature (700–800°C). Note that OMC is a rare example of processes in which the selectivity in partial oxidation products increases with temperature. The rigid conditions provide that the key OMC intermediate passes into the gas phase and also prevent deep oxidation of $CH_3^{\cdot}$ with oxygen. If O_2 is present in the gas phase, a methylperoxyl radical is formed:

$$CH_3^{\cdot} + O_2 \leftrightarrow CH_3O_2^{\cdot} \rightarrow CO_x + H_2O + H^{\cdot}.$$

At relatively low temperature, $CH_3O_2^{\cdot}$ decomposes to give deep oxidation products, which sharply decreases the selectivity in ethane.

It should be borne in mind that OMC can also occur in the absence of catalysts. Gas-phase formation of ethane is preceded by the reaction of CH_4 and O_2 to form $CH_3^{\cdot}$ and $HO_2^{\cdot}$. According to our data, the yield of C_2H_6 in an empty reactor at 800°C выход was about 5%. Filling the reactor with quartz particles suppressed gas-phase OMC, probably, because methyl radicals decay on quartz surface. This fact provides evidence to show that OMC catalysts should not have a very developed surface. In what follows, relying on the results obtained at the IOC RAS, we consider correlations between the catalytic properties and composition of manganese systems.

Regularities in the Catalytic Action of Manganese Systems

Manganese oxide (Mn_3O_4) in the temperature range 600–800°C tends to accelerate deep methane oxidation only [75, 76]. The supported catalyst 10%Mn/Al_2O_3 exhibited a very low selectivity (S) in C_2 hydrocarbons: 2.6% at 750°C and the CH_4/air molar ratio 0.65. Replacement of Al_2O_3 by SiO_2 in the catalyst sharply increased the yield of C_2 hydrocarbons (from 0.4 to 6.3% at S = 31%). It should be emphasized that the activity and selectivity of Mn/SiO_2 systems depends on their Mn content and passes through a maximum at [Mn] = 10 wt %, which is probably explained by the fact that the oxidative properties change as Mn oxides react with support surface.

By studying the effect of alkaline additions on the properties of Mn catalysts we established that the strongest promoting effect is characteristic of Na [77]. Introduction of 4% of Na into 10%Mn/SiO_2 increased the yield of C_2 hydrocarbons [$B(C_2)$] at 800°C more than 2 times (from 8 to 16.9%) by increasing the conversion of CH_4 (from 16.9 to 23.9%) and selectivity (from 48.6 to 70.5%).

The nature of alkaline promoter affects the catalytic activity. With a Li-doped sample, the overall CH_4 conversion also increased (to 25.4%), but the selectivity slightly decreased, as $B(C_2)$ increased to as little as 11%. Additions of other alkali metals (K and Cs) appreciably increased $S(C_2)$ (to 53–63%), but the CH_4 conversion therewith decreased. Alkaline modification of Mn/SiO_2 also affects the C_2H_4/C_2H_6 ratio in the OMC products. The largest fraction of C_2H_4 in the resulting C_2 hydrocarbons (>90%) was observed on the catalyst (10%Mn + 4%Na)/SiO_2.

A promoting effect in Mn/SiO_2 systems was also observed with chlorides [77]. Sodium fluoride (unlike CH_3COONa) only slightly affected the properties of Mn/SiO_2. With a NaCl-containing samplem the strongest (25.8%) effect on the yield of C_2 hydrocarbons was observed. Replacement of NaCl by NaBr in this catalyst slightly decreased the conversion of CH_4 into C_2 hydrocarbons (to 19.2%). The OMC products formed on the NaCl- and NaBr-containing catalysts contained ethylene as the major component. According to [1, 77], the enhanced catalytic activity is associated not only with the suppression of deep oxidation centers, but also with the involvement of $Cl^{\cdot}$ in certain OMC stages. These radicals are formed by high-temperature composition of the chloride, and their reaction with CH_4 molecules gives rise to $CH_3^{\cdot}$ particles. Chlorine radicals are also able to abstract hydrogen from C_2H_6, favoring dehydrogenation of ethane into ethylene. Thus, the promoting effect of NaCl (and other halides) includes reaction with catalyst and appearance of new species active in hydrocarbon C–H bond cleavage.

The nature of the modifier strongly affects the state of Mn catalysts [4]. For example, under the action of Na^+ ions (from $NaCH_3COO$) the specific surface area of the support sharply decreases (to < 1 m^2 g^{-1}), and α-crystoballite (SiO_2) and braunite (Mn_2O_3) phases form. NaCl favors decreased cocking and crystallization of the support: The prevailing phases in the chloride catalyst are hallite (NaCl) and braunite. Promoting Mn/SiO_2 affects the nature of oxygen desorption and shifts the oxygen release maximum to higher temperatures (from 500–800°C to 650–900°C). Decreased mobility of lattice oxygen is likely to enhance catalyst selectivity.

Garbuzyuk et al. [78] used the example of the most efficient catalyst (Mn + $NaCl/SiO_2$) to explore one of the most challenging problems of OMC, associated with that the highest possible yield of C_2 hydrocarbons is within 25–30% and depends on the relative rates of formation and deep oxidation of C_2 hydrocarbons [5]. Table 2 lists the results of oxidation of CH_4 + C_2H_6 mixtures. As seen, if the starting mixture contains up to 11 vol %, no appreciable increase of ethane and ethylene in the products. This finding shows that C_2H_4 is formed from C_2H_6 and implies that the limiting concentration of C_2 hydrocarbons in OMC products is about 9–11%. In the presence of Mn + $NaCl/SiO_2$, the major oxidation product is CO, and its concentration compares with that of C_2H_4. This circumstance makes such mixtures promising starting materials for oxosynthesis, for example, for manufacturing pro-

Table 2. Oxidation of methane–ethane mixtures on the Mn+NaCl/SiO_2 catalyst [78]; [740°C, (CH_4 + C_2H_6):O_2=3:1, 5000 h^{-1}

Fraction of C_2H_6 in the mixture, vol %	Composition of gaseous products, vol %[a]							
	CH_4	C_2H_6	C_2H_4	C_3H_6	CO	CO_2	O_2	H_2
1.2	69.1	1.4	10.2	0.42	10.2	4.1	0.26	1.6
5.6	67.2	1.6	9.2	0.34	13.2	2.4	0.16	2.5
11.0	63.1	1.5	8.0	0.35	16.7	2.6	0.04	7.0
31.6	37.7	6.0	15.5	0.49	18.3	2.2	0.05	18.5

[a] The data were obtained 15 min after beginning of the experiment.

pionic acid, which can favor more efficient oxidative reforming of natural gas.

Oxidative Properties of Mn Catalysts

The contribution of the lattice oxygen in Mn systems into oxidative transformations of CH_4 was studied by the pulse technique, which made it possible to determine the quantity of oxygen in the catalyst, capable of reacting with methane, and the selectivity of formation of oxidation products at various CH_4/O_{cat} ratios [4, 79, 80].

In the absence of gaseous O_2 at 500–600°C, no other processes than deep methane oxidation was observed on the catalysts 2–20% Mn/SiO_2; C_2 hydrocarbons are formed at high temperatures only (700–800°C). With pure MnO_x, deep methane oxidation was observed exclusively over the entire temperature range. The Mn + Na/SiO_2 system contains almost no active oxygen, whereas Mn + NaCl/SiO_2 catalysts are highly efficient in OMC at 800°C [CH_4 conversion and $S(C_2H_4)$ are 26 and 78%, respectively]. Active oxygen measurements in MnO_x, Mn/SiO_2, and Mn+NaCl/SiO_2 showed that the O/Mn molar ratio in these systems is almost independent of their composition and spans the range 0.21–0.31 (at 800°C). These values imply reduction of Mn_3O_4 to MnO. It was shown that SiO_2 and NaCl suppress deep oxidation, which is primarily associated with a change in the state of active oxygen, rather than with a decrease in its concentration (Fig. 1).

Correlations between contact time and CH_4 conversion and the selectivity of formation of CO_x and C_2 hydrocarbons were established in experiments with Mn + NaCl/SiO_2 samples of various weight (Fig. 2).

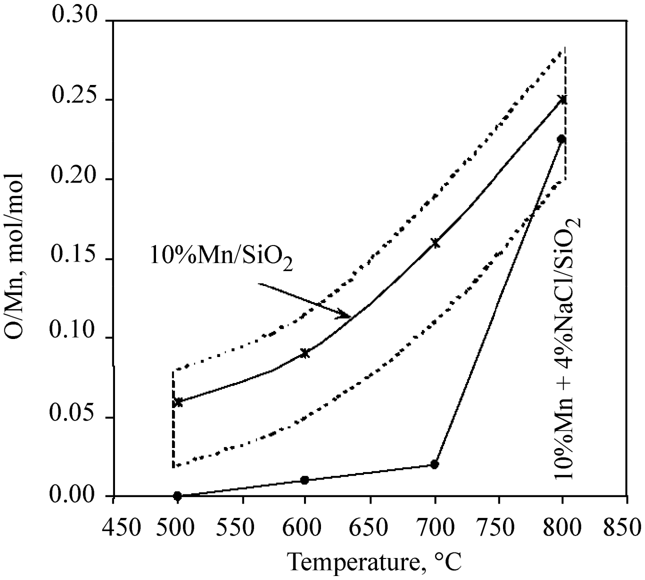

Fig. 1. Temperature dependences of the O/Mn molar ratio on supported catalysts [80]. Dashed lines show the O/Mn range for 2–20% Mn/SiO_2 catalysts.

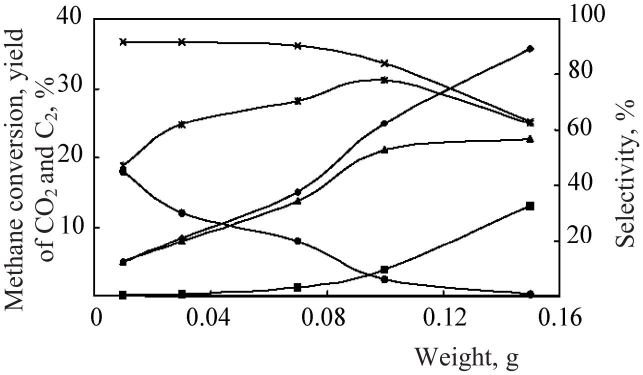

Fig. 2. Dependence of parameters of the oxidative dimerization of methane in the pulse mode on catalyst weight [4]. Yield: (♦) CH_4, (■) CO_x; and (▲) C_2 hydrocarbons. Selectivity: (×) C_2; (*) C_2H_4; and (•) C_2H_6. Temperature 800°C; methane pulse volume 1.3 ml; catalyst 10%Mn + 4%NaCl/SiO_2.

One can clearly see in the figure the range of the highest selectivity (85–91%), when the fraction of ethylene in C_2 hydrocarbons is higher than 80% (samples 0.07 and 0.10 g). It is noteworthy that the yield of C_2 hydrocarbons is close to limit (~25%), like under catalysis conditions. The fact that the yields of C_2 hydrocarbons in the oxidation of CH_4 with gas-phase and lattice oxygen are close to each other imply that the maximum yield of OMC products is controlled primarily by the reactivity of CH_4 and C_2 hydrocarbons, rather than the nature of the oxidant.

Further evidence for the correlation between the catalytic and oxidative properties of Mn+NaCl/SiO_2 systems is provided by the prevalence of CO between the carbon oxides formed in the pulse mode [4]. Moreover, these systems can perform OMC if the methane pulse contains much CO: up to 50 vol %. As mentioned above, CO can be involved in joint processing with C_2H_4. The formation of CO in preference to CO_2 offers further advantage of reducing the total heat effect of the process and involving more completely lattice oxygen in forming C_2 hydrocarbons. The latter applies for the OMC mode with alternate contact of Mn systems with air and methane.

Prospects of Practical Use of OMC

Over the past years the previous enormous interest in the direct synthesis of ethane and ethylene from methane [5, 6] has given the way to less research efforts in this field in view of the low economic efficiency of the OMC process. After 2005 the most interest to OMC has come from China and Iran.

Various manganese systems still remain the most efficient OMC catalysts [81–89]. Hou et al. [81] showed that modification of Mn/SiO_2 with sodium salts with various anions (WO_4^{2-}, MoO_4^{2-}, SO_4^{2-}, PO_4^{3-}, $P_2O_7^{4-}$, CO_3^{2-}, and SiO_3^{2-}) enhances the reducibility of the active components and the yield of C_2 products. This is explained by the crystallization of the amorphous SiO_2 into α-crystoballite and Mn_2O_3 formation. Wang et al. [82] made use of the zol–gel technique to prepare 5%Na_2WO_4–2%Mn/SiO_2 and could reach a 30% methane conversion at $S(C_2)$ = 70%. Wu et al. [83] in their study on the promoting effect of La additions found that the most efficient is joint application of La and Mn. In the presence of 5% Na_2WO_4/2%La–2%Mn/SiO_2 at 800°C, the process selectivity and the yield of C_2 hydrocarbons were 56 and 25%, respectively, at C_2H_4/CO = 1. Thien et al. [88] reported a very high yield of C_2 hydrocarbons (32.24% at the methane conversion 40.55%) on a Na–W–Mn/SiO_2 catalyst at 850°C and the volume rate of the reaction mixture 24 l g^{-1} h^{-1} (CH_4/O_2 = 7.4).

Not only Na, but also Li is a suitable alkaline addition to the W–Mn/SiO_2 system [87]. Malekzadeh et al. [89] found that the catalytic activity and selectivity of transition metal catalysts Na_2WO_4–MO_x/SiO_2 (M = V, Cr, Mn, Fe, Co, or Zn) depend on their surface morphology, texture characteristics, and ability to undergo reduction. Manganese exhibits a much higher activity (V ~ Cr ~ Zn ~ Fe ~ Co < Mn) and selectivity (V ~ Cr ~ Fe ~ Co ~ Zn < Mn) than the other elements studied. Temperature-programmed reduction, X-ray phase analysis, and scanning electron microscopy were employed to reveal the nature of interactions of the components of the catalysts both with the support and with each other, which, according to the authors of [89], which determine the catalytic properties of systems like Na_2WO_4–MO_x/SiO_2.

Research on other known OMC catalysts [5] has also been continued. Amin and Pheng [90] performed optimization of the process on the Lansford catalyst Li/MgO. The maximum yield of ethylene (8.14%) was observed at 840°C and the volume feed rate of the reaction mixture containing 18.9 vol % of oxygen equal to ~20 l g^{-1} h^{-1}. With systems on the basis of CaO, modified by rare-earth metals (La, Nd, Yb), the most active in OMC was an Nd_2O_3–CaO catalyst (Nd/Ca = 0.05) in whose presence the methane conversion was 19.5% at the selectivity 70.8% [91].

Lee et al. [92] synthesized by the zol–gel technique and tested in OMC perovskites $LaMO_3$ (M = Fe, Co, Ni). According to Rodulfo-Baechler et al. [93], successive modification of La_2O_3 with Ni and Sr oxides gives the system 2 mol % Ni/$La_{0.98}Sr_{0.02}O_x$ which contains oxygen vacancies and included mixed oxide La_{2-x}·Sr_xNiO_4 particles.

For enhanced efficiency of methane processing Zhang et al. [85] suggested a new combination of OMC with CH_4 reforming to syngas. The simultaneous production of C_2 hydrocarbons, CO, and H_2 was performed in the presence of a Mn/Na_2WO_4/SiO_2. Under the optimal conditions, the C_2H_4:CO:H_2 ratio in the product mixture was 0.9:1:1, yield 11.6%, selectivity 68%; at the same time, the selectivity in CO_2 was as low as 16.1%. According to the authors of [85], the resulting mixture is suitable for the synthesis of propanal by hydroformylation.

An improved version of the approach to methane processing involves the use of a two-layer catalyst [86]. To avoid excessive oxygen consumption, a layer of a moderate activity catalyst (Co/Al_2O_3) and a layer of $Na_2WO_4/Mn/SiO_2$ which is the most active OMC catalyst are placed one after the other. Product composition could be controlled by varying the weight ratio of the catalysts and reaction conditions. The maximum yield of CO and ethylene was 18.5%.

In a series of works [94–97], CO_2 was suggested as an oxidant for methane. The highest activity in this process was exhibited by manganese–cerium oxide systems promoted by CaO. The yield of C_2 hydrocarbons on 12.8% CaO/6.4%–MnO/CeO_2 was 3.9% at the selectivity 82.6%. It is suggested [96] that the basicity of the catalyst and its reducibility enhance activity of CaO-MnO/CeO_2 systems.

One of the problems of OMC is associated with a large heat effect of this reaction (174 kJ mol^{-1} C_2H_6). Taking into account that OMC occurs in parallel with deep oxidation, the problem of heat removal becomes still more serious. Hot zones can develop even in a laboratory reactor, as Wang et al. [98] observed at high volume feed rates of the reaction mixture (42 l h^{-1}, catalyst weight 1 g). It was found that oxidation of methane on $BaCO_3/La_2O_3$ is initiated, when the reactor has been heated to as low as 450°C, after which the temperature of the central part of the catalyst layer increases up to 750°C. Performing OMC in a boiling catalyst layer favors faster heat removal [99], even though in this case more rigid requirements to the mechanical strength of catalyst particles are imposed.

Over the past year there have been much efforts to develop oxygen-conducting membrane reactors for OMC [100–103]. Membranes on the basis of oxides of Ba, Sr, Co, and Fe [100], La, Sr, Co, and Fe [102], and Ba, Sr, Co, and Fe [103] have been tested. OMC occurred on walls of membrane tubes where no catalyst was placed. The use of membranes allows one to solve the problem of controlled delivery of oxygen to the OMC zone and thus makes the process safer. At the same time, this technology provides no gain in the limiting yields of ethane and ethylene (25–30%). According to [102], the maximum conversion of methane to C_2 hydrocarbons in the OMC process in a membrane reactor in the presence of a Sr–Ti–Li–O catalyst was 21%. In the context of the problem of oxygen release we would like to mention the work of Bostan et al. [104], who studied OMC in a periodic regime (alternate feeding of methane and air) on the $SrMnO_3$ and $SrCoO_3$ perovskites.

By now a huge body of data on OMC catalysts and mechanism of oxidative methane dimerization to C_2 hydrocarbons has been accumulated. However, the question of whether OMC is expedient to use in practice is still open. This is explained by a fairly low conversion of methane to ethane and ethylene (about 25%), which depends on the equalization of the rates of oxidation of CH_4 and C_2 hydrocarbons in the presence of various oxidants (O_2, N_2O, CO_2, catalyst oxygen). As follows from our estimates, the yield of OMC products can be increased to 40% in a two-stage process, when, as the first stage, fairly stable methane derivatives, for example, $CH_{4-x}Cl_x$, are obtained and then a mixture of CH_4 and $CH_{4-x}Cl_x$ is processed in the absence of oxidants to obtain C_2 and other hydrocarbons. Utilization of the HCl formed allows the two stages to be closed into a catalytic cycle. The fact that the yield of OMC is improved by 10–15% makes this technology more competitive with respect to the presently existing industrial technologies for the production of ethylene from oil stock.

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