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Gas-phase oxypyrolysis of light alkanes

V S Arutyunov, R N Magomedov

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Abstract. The published studies in a quickly developing field of research, gas-phase oxidative pyrolysis (oxidative cracking, oxidative dehydrogenation) of light alkanes, are systematized and analyzed. This process attracts researchers' attention due to the general enhancement of interest in the kinetics of homogeneous-heterogeneous processes of partial oxidation of hydrocarbons and also in view of the prospects for the design of new industrial processes based on light hydrocarbons as raw materials. The bibliography includes 87 references.

I. Introduction

Pyrolysis, cracking and dehydrogenation are basic processes of petrochemistry. However, high power intensity of industrial processes based on these highly endothermic reactions, especially those using light feedstock (natural and associated gas components), stimulates permanent interest of researchers in oxidative conversion of hydrocarbons.[1–5] Partial oxidation of hydrocarbon feedstock is the most efficient way of energy supply needed for these processes. The oxidative conversion of light alkanes to basic chemicals poses great potential for technological development, and progress in this area may crucially affect the modern petrochemistry. However, the advantages of these reactions demonstrated by now are still insufficient to convince manufacturers to replace reliable, well-developed production processes by new ones. Considerable effort is required for their further investigation and improvement.

Unlike thermal pyrolysis, in the oxidative pyrolysis preheated hydrocarbons react with oxygen. The heat needed to increase the temperature of the reaction mixture to ensure at least partial decomposition of hydrocarbons comes from exothermic oxidation reactions occurring directly in the reaction zone. This decreases the intensity of heat exchange through the reactor walls and, hence, the associated heat loss, and makes the requirements to reactor material less stringent. The possibility to attain higher temperatures of the reaction mixture inside the reactor makes it possible to shorten the process time and, hence, either decrease the reactor size or enhance the feedstock conversion.

The addition of even a minor amount of oxygen to the feedstock considerably increases the productivity of pyrolysis. Heat evolution, directly in the reaction zone, due to partial oxidation of hydrocarbons accompanied by generation of highly reactive $OH^{\bullet}$ radicals sharply enhances the system reactivity. For example, even stabilized gas condensate containing up to 50% of methane can undergo a 50% conversion in only a single pass through the reactor.[6] By supplying a sufficiently large amount of oxygen, it is possible to switch to autothermal operation.

Apart from the obvious advantages regarding heat supply to the reacting system, thermodynamic limitations on the product composition can in some cases be circumvented by means of oxidative processes. For example, according to the equilibrium constant, the quasi-equilibrium conversions of ethane and propane corresponding to the rapidly establishing quasi-equilibrium between n-alkane and the corresponding monoalkene are $<1\%$ at temperatures below 400 °C, whereas in the oxydehydrogenation, the quasi-equilibrium alkane conversion reaches almost 100% at the same temperature.[7] The oxidative dehydrogenation also makes it possible to avoid many problems associated with soot formation. Studies of oxidative dehydrogenation are stimulated by faster (as compared with ethylene) growth of the demand of propylene, the yield of which in the pyrolysis or catalytic cracking of hydrocarbon feedstock is low. Therefore, the development of effective oxidative processes for the production of basic chemicals from ethane and propane, the more so from methane, could crucially affect modern petrochemistry.

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

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The oxidative pyrolysis (oxypyrolysis) of alkanes, special cases of which are oxidative cracking (oxycracking) and oxidative dehydrogenation (ODH), has long been used in industry to produce large-tonnage products such as acetylene, carbon black, synthesis gas and hydrogen. In the 1960s, numerous studies were performed considering the oxidative pyrolysis of light petrols to alkenes as an alternative to popular thermal pyrolysis. However, serious drawbacks of the process — greater consumption of the feedstock (expensive naphtha) and the necessity to separate more complex product gas mixtures, which contain, apart from methane, hydrocarbons and hydrogen, also carbon oxides (CO, CO_2) and oxygen-carried impurities — make this process less economic compared to thermal pyrolysis.

Nevertheless, the interest in the oxidative dehydrogenation as a potential route to alkenes grows following an increase in the world consumption of alkenes and transition to more 'rigorous' processes due to increasing share of light feedstock. However, the catalytic dehydrogenation of alkanes has been widely used for this purpose as long as since the 1930s, whereas the currently available data on oxidative dehydrogenation are still insufficiently attractive for commercialization.[7]

The equilibrium constant for alkane dehydrogenation to monoalkene rapidly decreases following a decrease in the carbon backbone length, while the temperature needed to achieve a particular conversion correspondingly increases. For example, a 40% equilibrium conversion of dodecane is achieved by heating it to 450 °C, while propane has to be heated to 580 °C to achieve the same equilibrium conversion, and in the case of ethane, this temperature is 700 °C (Fig. 1). However, the rates of side processes, soot formation and catalyst deactivation also rapidly increase at these temperatures.[7] Therefore, a beneficial feature of oxypyrolysis (oxydehydrogenation) is the possibility to avoid at least some of these problems.

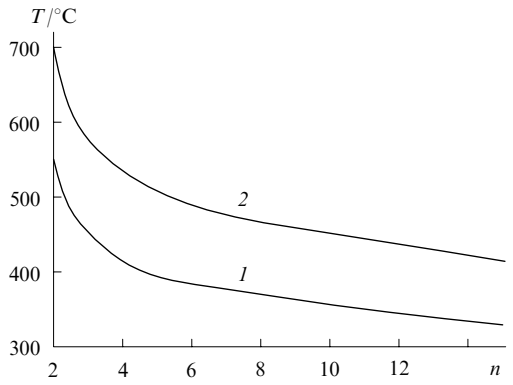


Figure 1. Temperature needed to achieve 10% (*1*) and 40% conversion (*2*) of C_n alkanes ($n = 2-15$) by the reaction n-alkane ⇄ monoalkene at $p = 1$ atm.[7]

Interesting prospects of oxidative pyrolysis and, in particular, oxidative dehydrogenation were opened up by studies dealing with the use of high-temperature processes with short time (~1–10 ms) contact with the catalyst. The catalyst can be supported on a monolithic (honeycomb) material or manufactured as gauzes or pellets. Under these conditions, a 70% ethane conversion was achieved on platinum-coated ceramic foam at ~1000 °C, the selectivity towards ethylene being up to 65%. The mechanism that is now supported by most of researchers implies a considerable contribution of homogeneous processes, the role of the catalyst being mainly reduced to initiation of the reaction and generation of heat needed for the reaction to proceed (see Section III.4). Despite the alluring prospects of such process arrangement, there are still some unsolved issues hampering its practical implementation, which are related to catalyst durability, temperature control and safety.

The vast majority of published studies dealing with oxypyrolysis of light alkanes were performed as catalytic studies, although many authors noted a considerable contribution of homogeneous processes, especially at high temperature, and paid much attention to them. With transition to light alkanes present in hydrocarbon gases, the increase in the characteristic oxypyrolysis temperatures forces researchers to consider homogeneous-heterogeneous processes. Furthermore, in some cases, gas-phase reactions clearly predominate. Due to the known advantages of non-catalytic reactions as regards the requirements to feedstock preparation, equipment, catalyst supply and regeneration and process stability, the potential transition to gas-phase reactions appears attractive.

The principal goal of this review is to give a systematic account of the recent published data on gas-phase oxypyrolysis of light alkanes C_1-C_6 comprised in natural and associated gases. Certainly, it is impossible to avoid comparison with the corresponding catalytic processes, the more so, because heterogeneous reactions undoubtedly make a noticeable contribution to these, generally homogeneous-heterogeneous reactions. However, the presence of up-to-date comprehensive reviews on the catalytic oxypyrolysis and oxydehydrogenation of light alkanes (see, for example, Ref. 8) makes this task easier, because there is no need to dwell into specific details of catalytic processes.

Note also some other closely related fields that are hard to separate from the considered subject matter, but that we nevertheless tried not to consider in this review. The gas-phase oxidative pyrolysis of light alkanes is a special case of incomplete (partial) oxidation of hydrocarbons in the medium-temperature range (~300–1000 °C), its mechanism being closely intertwined with the mechanisms of oxidative condensation of methane, partial alkane oxidation to oxygenates and to synthesis gas. However, due to the presence of a huge array of publications dealing with these processes (see, for example, Ref. 5 and the references cited therein), they are not considered in this review.

Formally, processes using H_2O (steam reforming) and CO_2 (carbon dioxide reforming) as oxidants can also be assigned to oxidative pyrolysis. According to Bhasin *et al.*,[7] the use of CO_2 as the oxidant for ethane dehydrogenation ensures a decrease in temperature compared with pyrolysis and higher values of ethane conversion and selectivity of ethylene formation compared with other methods used to obtain ethylene from ethane. However, in reality, this highly endothermic process takes place only in the presence of a catalyst; therefore, it is also beyond the scope of this review.

Finally, the review scarcely touches upon the kinetic modelling of alkane oxycracking. In recent years, interesting studies containing detailed kinetic models of the oxidative conversion of C_1-C_4 alkanes and heavier fractions at medium temperatures were published.[9–13] For verification of these models and bringing them to the level of an

analytical tool with a high predictive potential, much is still to be done to coordinate the results of modelling with the existing array of reliable experimental data, collection of which was the key goal of the review.

Since the production of alkenes is not the major topic of this review, we replaced the term 'oxidative dehydrogenation' used in most of the considered studies by a more general term, 'oxidative pyrolysis' (oxypyrolysis), which (unlike the term 'oxidative cracking') is applicable to any light alkane including methane. From the mechanistic standpoint, all of these processes can be regarded as specific cases of more complex process, partial oxidation of alkanes in the medium-temperature region.[5]

II. Oxidative pyrolysis of methane

The specific features of methane pyrolysis[14] and oxypyrolysis as compared with analogous conversion processes of other alkanes are obvious. However, it is for this least typical and most stable alkane that the main advantages of oxypyrolysis over thermal pyrolysis are manifested most clearly, in particular, the possibility of autothermal operation of the process, at the expense of deep conversion of a part of hydrocarbon feedstock, and substantial lowering of the energy levels of intermediates with respect to the reactant energy. This can be clearly seen in the comparative diagram of the energy levels of the thermal and oxidative methane pyrolysis on a Pt catalyst (Fig. 2). Note that the activation energy for the rupture of not only the first but also all subsequent C—H bonds appreciably decreases. In both the catalytic and gas-phase processes, the presence of oxygen results in a marked decrease in activation energies for almost all steps of conversion of the starting hydrocarbons.

Apart from the technical carbon black production, another classical object for the comparison of thermal and oxidative pyrolyses of methane is acetylene production where natural gas is currently the major feedstock.

$$2\,CH_4 = C_2H_2 + 3\,H_2,\ \Delta Q = -90\ \text{kcal mol}^{-1}$$

The free energy of this reaction becomes negative at temperatures above 1500 K, *i.e.*, the acetylene formation becomes thermodynamically favourable. As the temperature increases, the free energy of acetylene formation, unlike that of other hydrocarbons, does not increase but decreases, and, hence, the thermodynamic stability at temperatures above 1100 K is higher for acetylene than for other hydrocarbons. However, at even higher temperatures, acetylene decomposes to give carbon black and hydrogen (Fig. 3).

$$C_2H_2 \rightleftharpoons 2\,C + H_2$$

Therefore, the contact times in acetylene production are very short and the products are rapidly quenched. This is a typical example of industrial use of non-equilibrium kinetics for obtaining high yields of the intermediate product of pyrolysis. According to experimental data, decreasing the partial pressure of methane by diluting it with inert diluents leads to higher yields of acetylene.

The acetylene production processes in industry differ by the ways of heat supply and product quenching. Apart from oxidative pyrolysis (thermooxidative cracking), acetylene is produced by pyrolysis in regenerative type fixed-bed reactors where the packing is alternatively heated by combustion products and gives-off heat to the reactants; pyrolysis

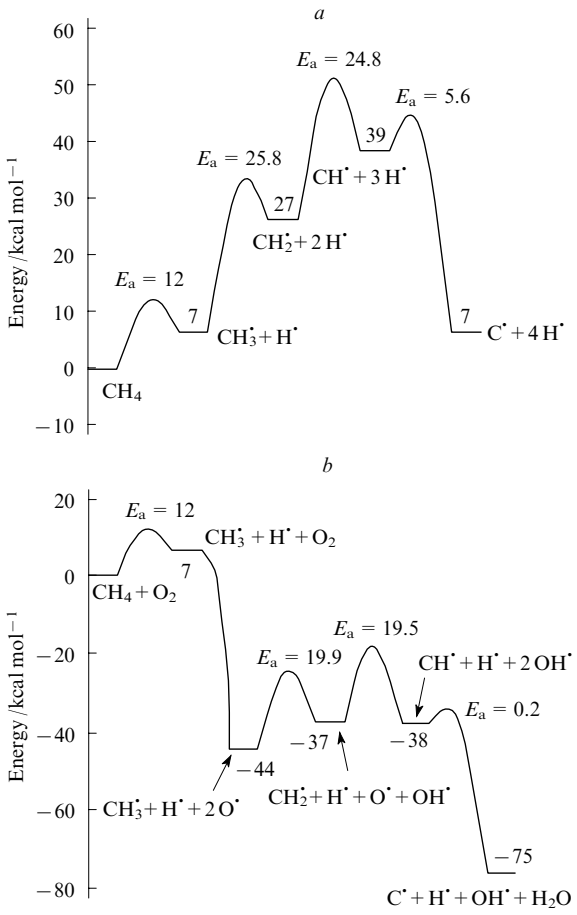


Figure 2. Energy level diagram of thermal (*a*) and oxidative (*b*) pyrolysis of methane on a Pt catalyst.[15]

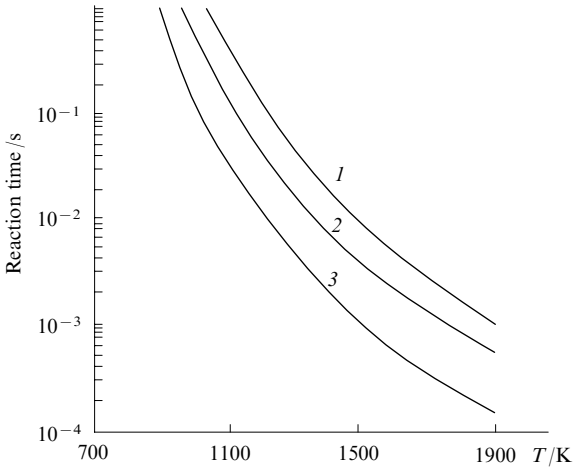


Figure 3. Time of acetylene decomposition *vs.* temperature at different conversions (ε) and initial concentrations of acetylene ($[C_2H_2]_0$).
ε = 10%, $[C_2H_2]_0$ = 10 vol.% (*1*), ε = 10%, $[C_2H_2]_0$ = 20 vol.% (*2*), ε = 3%, $[C_2H_2]_0$ = 10 vol.% (*3*).

in a stream of a gaseous heat transfer medium (homogeneous pyrolysis); pyrolysis with heat transfer through the reactor wall (in tubular furnace); electrocracking of hydrocarbon gases and pyrolysis in a low-temperature plasma stream. In terms of the chemical mechanism, these processes can be split into three groups: thermal pyrolysis, oxidative pyrolysis and electron discharge processes.

The main idea of oxidative pyrolysis is the use of exothermic oxidation to provide the endothermic pyrolysis with energy. High temperature is maintained during oxidative pyrolysis due to combustion of CH_4, which occurs in the same zone as methane cracking. In the deficiency of oxygen (partial oxidation at $CH_4 : O_2 = 0.65$) and at high temperature ($\sim$1500 °C), the process is described by the overall reaction

$$6\,CH_4 + 4\,O_2 = C_2H_2 + 8\,H_2 + 3\,CO + CO_2 + 3\,H_2O;$$

the formation of acetylene starts only in the zone that is almost devoid of oxygen. As in the partial oxidation of methane to synthesis gas, in the first stage of oxidative pyrolysis, methane is rapidly oxidized to fully consume the deficient oxygen and to give deep oxidation products, carbon dioxide and water. Other products, including acetylene, are formed in the second stage, thermal pyrolysis in the absence of oxygen. The autothermal mechanism of the process is provided by a combination of the exothermic and endothermic reactions; moreover, heat is evolved directly in the same reactor where it is to be consumed, which eliminates the problem of heat transfer through the walls. The subsequent decomposition of acetylene to carbon black and hydrogen is prevented by quenching the reaction (flame) by injecting cold water.

Only 23% – 25% of methane is spent for acetylene synthesis, while the main bulk of methane is spent for maintaining a temperature of about 1500 °C at which unoxidized methane is converted to acetylene and hydrogen. For achieving this temperature, much less oxygen is required than for complete oxidation: 0.6 m^3 of oxygen per m^3 of methane. The whole reaction occurs in the flame, and the final reaction products contain, apart from acetylene and hydrogen, also carbon oxides, water, ethane, acetylene homologues and carbon black.

The reactor design should ensure stable combustion of a hydrocarbon-rich methane – oxygen mixture occurring actually at the ignition limit. In addition, of considerable significance is homogeneous distribution of the evolved heat throughout the reactor volume, which is achieved by thorough stirring of the reactants being fed. Thus, there are the same problems as are faced by the oxidative conversion of methane to synthesis gas, though in a somewhat different range of conditions. A typical reactor design is presented in Fig. 4.

A hydrocarbon gas and oxygen pre-heated to $\sim$600 °C are separately fed to a mixing chamber where they are completely mixed. Then the mixture passes through a multichannel burner plate to enter the reaction chamber where owing to partial combustion of methane, the remaining methane is pyrolyzed. For safe reactor operation, the velocity of the methane – oxygen mixture must be much higher than the flame propagation velocity ($\sim$100 cm s^{-1}). The temperature of pyrolysis reaches 1450 – 1500 °C. The reaction duration is 0.003 – 0.01 s. The mixture is quenched at the outlet by water injection. The gas yielded from the oxidative pyrolysis of methane contains up to 14 vol.% of

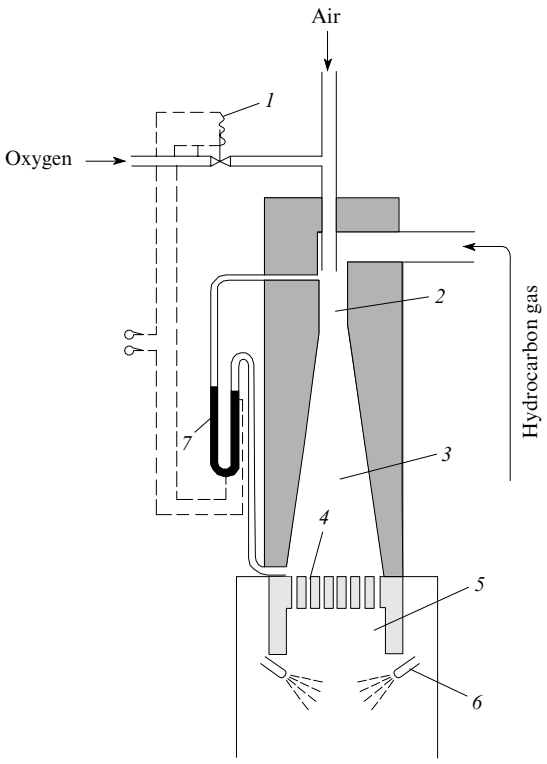


Figure 4. Scheme of the BASF reactor for acetylene production by oxidative pyrolysis.[3]
(*1*) Oxygen feed valve; (*2*) neck; (*3*) mixing chamber; (*4*) burner plate; (*5*) reaction chamber; (*6*) quench nozzles; (*7*) manometer.

acetylene, up to 5 vol.% of hydrogen and up to 28 vol.% of carbon monoxide, *i.e.*, it may simultaneously serve as a source of synthesis gas.

Other industrial processes based on oxidative pyrolysis of methane are also being developed. For example, the production process of ethylene and liquid hydrocarbons based on homogeneous oxidative pyrolysis of methane to acetylene and hydrogen was implemented on a pilot scale (Fig. 5).[16] The oxidative pyrolysis occurs at high temperature at the expense of combustion of a part of methane in oxygen. The acetylene and hydrogen thus formed are routed to catalytic hydrogenation to give ethylene. Then two pathways are possible. The isolation of ethylene as the final product, *viz.*, the 'gas to ethylene' (GTE) process, can be regarded as an alternative to the oxidative condensation of methane. The other pathway, *viz.*, catalytic oligomerization of the obtained ethylene to a mixture of liquid hydrocarbons corresponding to aviation petrol with an octane number (ON) of 96 is an alternative to the 'gas to liquid' (GTL) process based on the Fischer – Tropsch reaction. The resulting mixture contains up to 50% of aromatic compounds but the benzene concentration is low. Actually, the problem of low ethylene yield upon methane pyrolysis has been solved in this process by introducing an additional step, namely, the catalytic hydrogenation of acetylene.

Processes where hydrogen is the major target product of methane pyrolysis are also being developed, for example, the Kvaerner KCB&H (Kvaerner Carbon Black and Hydrogen) process based on the reaction

$$CH_4 \longrightarrow C + 2\,H_2$$

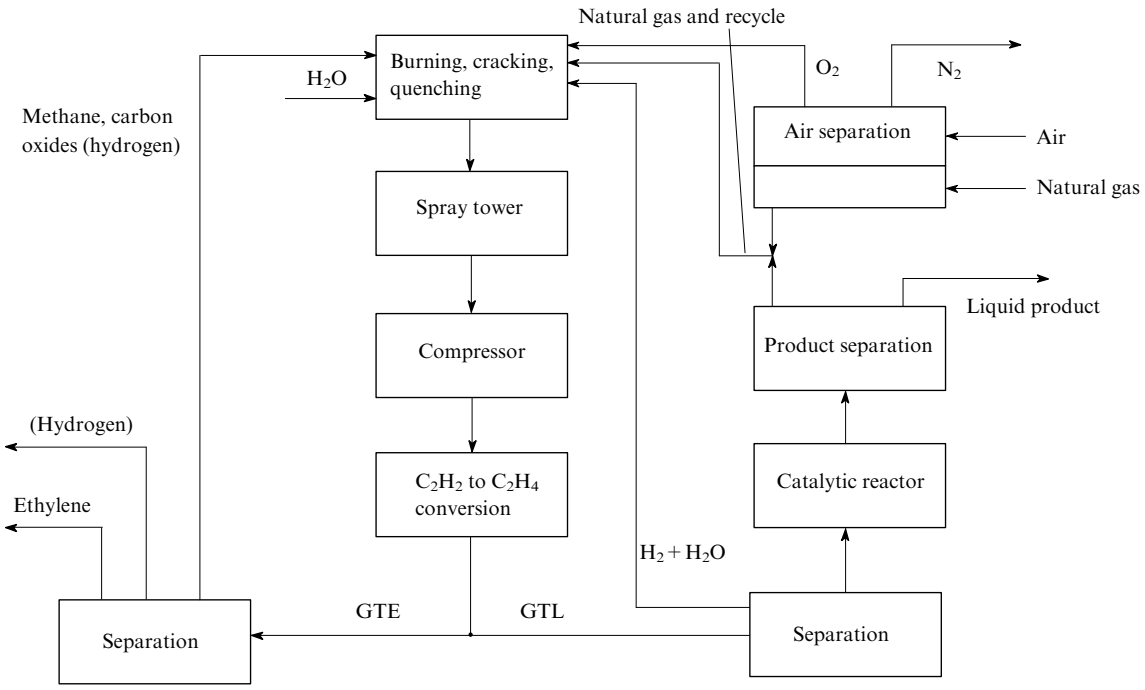


Figure 5. Oxidative pyrolysis of methane to acetylene and hydrogen followed by ethylene (GTE) or liquid product (GTL) production.[16]

The first industrial plant started operation in 1999. For pyrolysis, plasmotron is used. The theoretical power consumption is 1 kW-h per m^3 of hydrogen, but the actual consumption is much higher.

A similar process of hydrogen and technical carbon coproduction by the same reaction but based on methane oxidative pyrolysis was also reported.[17] Conversion of 1 mole of CH_4 according to this slightly endothermic reaction requires additional 74.8 kJ, which can be produced by complete combustion of only 0.084 moles of methane.

III. Oxidative pyrolysis of C_2-C_4 alkanes

1. Early works

The industrial pyrolysis of ethane to ethylene, which is a highly endothermic process carried out in tubular furnaces at temperatures below 1200 K, is upgraded toward more stringent conditions, *i.e.*, higher temperatures and shorter reaction times, which promotes increase in the ethylene yield. This, in turn, requires large energy expenditure and effective heat transfer through the reactor walls and imposes serious requirements on the furnace coil material and the rate of coke deposition, which deteriorates the heat exchange. Therefore, the oxidative dehydrogenation of ethane and other light alkanes at the expense of heat that is evolved upon partial oxidation of the initial feedstock has long been considered as an attractive alternative to the endothermic thermal pyrolysis.

The first works in this area were carried out back in the 1940s – 1950s.[18,19] The oxygen content in the feedstock was brought to 34%, and the selectivity of ethylene formation reached 80%, the conversion per pass being 50% – 60%. In the autothermal pyrolysis of stabilized gas condesate containing ethane, propane and other hydrocarbons to give ethylene,[20] air was used as the oxidant at an oxygen : hydrocarbon molar ratio of 0.1 to 0.5. Among the oxidation products, minor amounts of aldehydes and organic acids, apart from CO, CO_2 and H_2O, were detected (Fig. 6). As the oxygen : ethane ratio increased, the yield of CO increased, while the yields of CO_2 and H_2O correspondingly decreased.

Similar dependences were also obtained for oxidative pyrolysis of propane. Probably, an increase in temperature and in the oxygen : hydrocarbon ratio results in higher contribution of the homogeneous partial oxidation, which gives CO as the major oxygen-containing product. Thus, low oxygen : ethane ratios are most favourable for high selectivity towards ethylene formation. Under these conditions, the yield of carbon oxides is moderate and most of the reaction heat comes from the formation of water, which

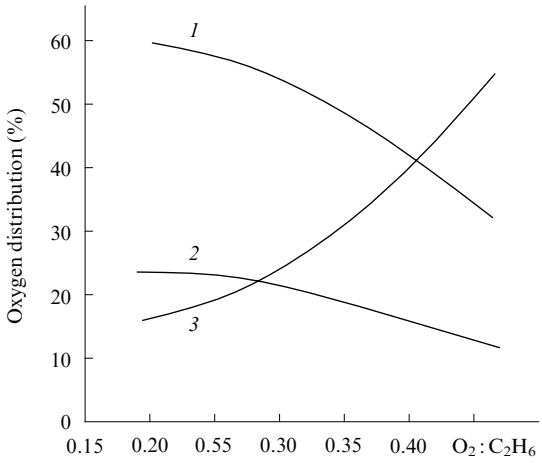


Figure 6. Oxygen distribution between the products of ethane oxidative cracking *vs.* oxygen : ethane ratio in the feed gas.[20] (*1*) H_2O, (*2*) CO_2, (*3*) CO.

counterbalances the endothermic pyrolysis of ethane to give ethylene and hydrogen:

$$C_2H_6 + 0.5\,O_2 \longrightarrow C_2H_4 + H_2O$$

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

If no carbon oxides are formed, the maximum ethylene yield according to these two reactions could be 3.448 molecules per O_2 molecule. The real situation is far from this. In addition, for sustainable oxidative pyrolysis of ethane, at any oxygen : ethane ratio, it is necessary to preheat the inlet gases to at least 565 °C. The effect of pressure on the process is noticeable but not critical. In the pyrolysis of ethane, pressure rise increases the yield of methane with respect to ethylene, while in the pyrolysis of propane, higher pressure promotes the formation of ethane with respect to ethylene. The effect on the yield of other components is minor. Therefore, the operating pressure should be determined most of all by economic reasons.

When the specified temperature has been attained, the process is completed over hundredths of a second and, hence, the reactor can be rather small. Even a fivefold increase in the residence time in the reactor does not noticeably affect the process. In the pilot process, a thermal efficiency of >80% was achieved, *i.e.*, the thermal loss due to oxidation of a part of ethane after recuperation of the effluent heat for heating the feed gas did not exceed 20%.

Table 1 and Fig. 7 present the concentrations of the products of autothermal pyrolysis of ethane, propane and a methane–ethane mixture obtained in the pilot unit.[20] The products were found to contain also traces of formaldehyde and acetaldehyde and smaller amounts of organic acids but their overall content <0.1%–0.2% of the initial hydrocarbon. The yield of aldehydes increases with a decrease in the hydrocarbon conversion. In addition to the higher flexibility and simplicity of the required equipment, the autothermal pyrolysis provides greater conversion of ethane per pass (up to 96% as compared with 50%–60% upon thermal pyrolysis) and allows using dilute mixtures with ethane content of not more than 50%.

Table 1. Products of autothermal pyrolysis of ethane and propane at different conversions (p = 1 atm).[20]

Products (except for H_2O)	Feed [conversion (%)]				
	ethane (52.6)	ethane (81.9)	propane (48.1)	propane (79.5)	mixture of CH_4, 37%, and C_2H_6, 63% (78)
H_2	15.8	19.8	8.8	9.6	18.3
CH_4	2.7	5.9	11.6	17.3	19.0
C_2H_2	0.05	0.3	0	0.3	traces
C_2H_4	19.6	21.3	12.5	18.0	16.7
C_2H_6	22.1	6.6	0.8	1.1	5.3
C_3H_6	0.7	0.6	6.6	5.1	0.3
C_3H_8			24.3	7.2	0.1
C_4	0.05	0.4	0.8	1.1	0.2
C_6	0	0	0	0.10	0
CO	2.1	4.5	4.2	4.9	5.5
CO_2	2.8	2.3	2.1	2.5	2.1
N_2	34.1	38.3	28.3	32.8	32.5
Total	100	100	100	100	100

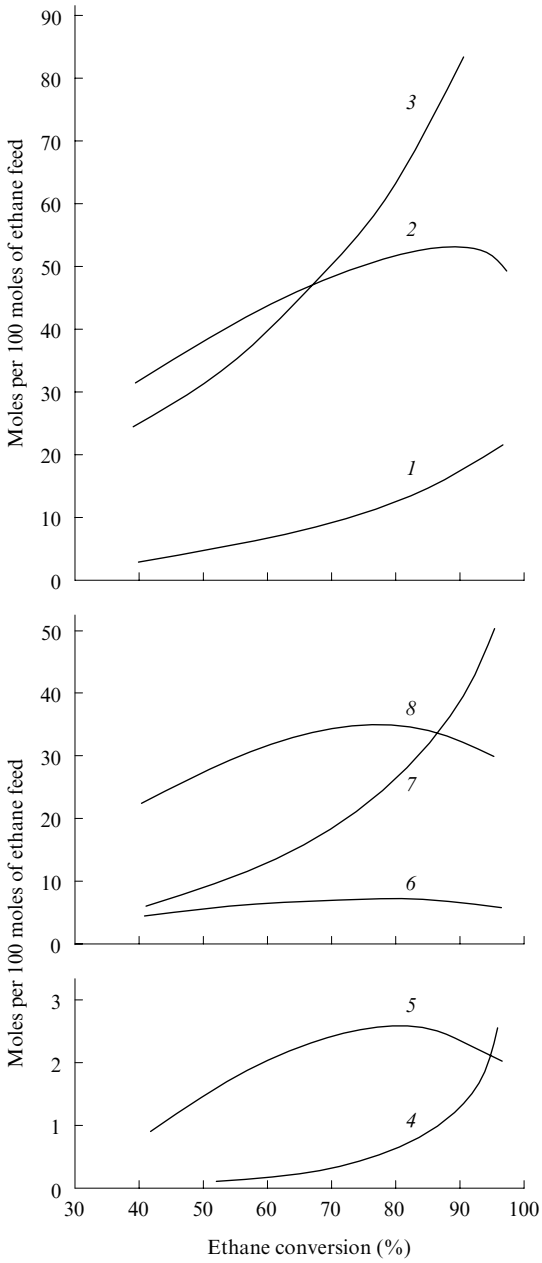


Figure 7. Yields of products of autothermal cracking *vs.* ethane conversion.[20]
(*1*) CH_4, (*2*) H_2, (*3*) ethylene, (*4*) acetylene, (*5*) C_3 and heavier hydrocarbons, (*6*) CO_2, (*7*) CO, (*8*) H_2O.

Satterfield and Wilson [21] carried out partial oxidation of propane under flow conditions at atmospheric pressure, a temperature from 350 to 475 °C, an oxygen to propane molar ratio ranging from 0.08 to 0.18 and the reaction time varying from 3.2 to 11.8 s. Apart from alkenes, carbon oxides and a minor amount of hydrogen, the effluent contained saturated hydrocarbons. Methane was the major saturated hydrocarbon, aside from unreacted propane. Also, the effluent contained ethane (methane : ethane ≈10 : 1) and traces of n-butane and isobutane. Water was the major condensible compound but methanol, aldehydes (mainly formaldehyde) and hydrogen peroxide were also

present. As the temperature increased, the yield of propylene with respect to the yield of oxygenates increased.

Despite the constructive simplicity and the possibility to use gases with high contents of methane and hydrogen, the oxidative pyrolysis has not yet found wide use and has only a minor share in ethylene production. Figure 8 shows one of the possible process flow diagrams. During the World War II, a small unit operated according to this scheme in Germany (Leuna Werke process) and had a 13 thousand tons per year capacity.[2] The process was carried out under vacuum (p = 410 Torr) at 850–885 °C. Thirty cubic meters of oxygen per 100 m^3 of ethane were fed to the reactor. The conversion per pass was 60%. The pyrogas contained ethylene (30%), hydrogen (26.5%), methane (7.0%), ethane (16%), propylene (2.5%), acetylene (1.5%), CO (10%), nitrogen (3%) and CO_2 (1.5%).

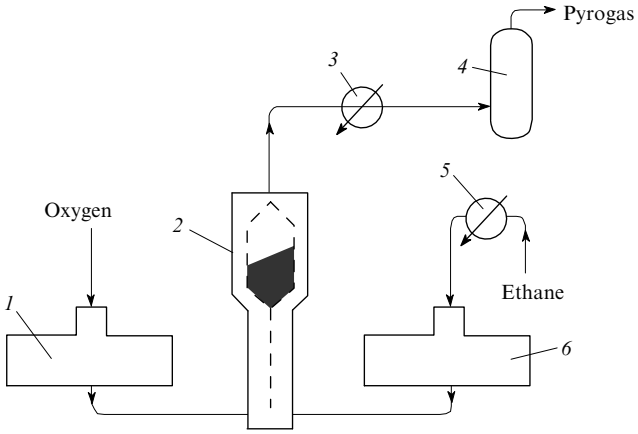


Figure 8. Flow diagram of the I G Farbenindustrie ethylene production by oxidative catalytic pyrolysis of ethane.[2]
(*1*) Heater, (*2*) cracking furnace, (*3*) tubular cooler, (*4*) quenching chamber, (*5*) steam preheater, (*6*) ethane preheater.

An oxidative pyrolysis process was also being developed in the Soviet Union.[22] In laboratory, oxidative pyrolysis of ethane produced 50 mass % of ethylene per pass and with recirculation, the process gave 70 mass % of ethylene with respect to the starting ethane. The oxidative pyrolysis of the propane fraction with a 95% propane content afforded 35.6% of ethylene and 13.5% of propylene. Upon pyrolysis of n-butane, 37.3% of ethylene, 15.8% of propylene and ~4% of liquid products were obtained. In the oxidative pyrolysis of natural gas petrol, the ethylene yield was 32.8%, the yield of propylene was 3.4% and that of butylene was 1.7%. Simultaneously more than 12.5% of lower aromatic hydrocarbons and ~2% of naphthalene were obtained. The exhaust gas formed in the ethane fraction pyrolysis contained, after isolation of ethane and ethylene, 25 vol.% of CO, 61 vol.% of hydrogen and 14 vol.% of methane, *i.e.*, it actually could serve as feedstock for the isolation of synthesis gas. On the basis of these investigations, the thermal pyrolysis unit at the Salavat refinery, which was fed by low-octane petrols and the butane fraction, was revamped for performing the oxidative pyrolysis. The oxidative pyrolysis of this feedstock gave up to 5% of aromatic hydrocarbons. No soot was observed, and the yield of oxygenates, aldehydes and acids did not exceed 0.02%–0.04%.[22]

Thus, despite a number of obvious advantages and the long history of attempts at industrial implementation of light alkane oxypyrolysis-based processes, the process flow charts proposed by now turned to be insufficiently attractive for wide use.

2. Effect of small oxygen additives

The pronounced acceleration effect of small oxygen additives on the pyrolysis of light alkanes was noted back in early-period works. Indeed, it was reported[23] that at p = 200 Torr, a temperature of 470–550 °C and oxygen concentrations of 0.015% to 2.51%, small oxygen admixtures considerably increase the initial rate of thermal decomposition of butane. As the amount of added oxygen increased, the efficiency of its action decreased, and at >1% of oxygen, the rate did not increase any longer. Also, the initial cracking rate of pure propane and a C_3H_8 + 20% NO mixture at a total pressure of 50 Torr was found to increase upon the addition of <2 Torr of oxygen.[24] Treatment of the quartz reactor surface with HF considerably enhanced the effect caused by the addition of oxygen. However, the increase in the amount of oxygen to >2 Torr did not cause further increase in the cracking rate (Fig. 9).

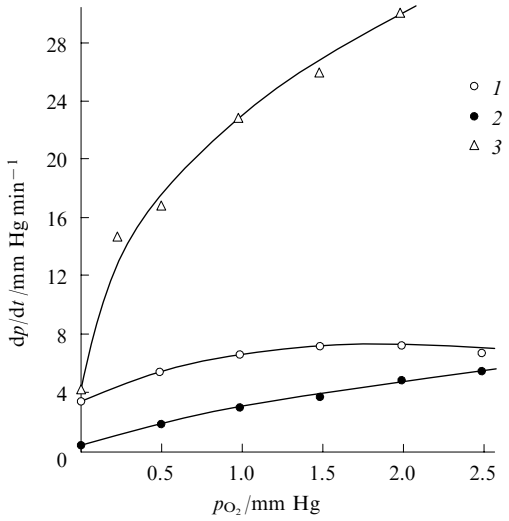


Figure 9. Initial cracking rate of C_3H_8 and a C_3H_8 + 20% NO mixture *vs.* oxygen admixture at 600 °C and p = 50 Torr.[24]
(*1*) C_3H_8 (no reactor pretreatment); (*2*) C_3H_8 + 20% NO mixture (HF pretreated reactor); (*3*) C_3H_8 (HF pretreated reactor).

The effect of minor admixtures of oxygen on the thermal cracking of n-butane was studied in a flow microreactor under atmospheric pressure, at a temperature from 500 to 630 °C and at conversion of <1% to minimize the effect of secondary processes.[25] The microreactor of diameter ~1.55 mm and with a length of 30 cm was manufactured from glass, which was chosen in view of its inertness towards oxygen in order to minimize the surface effect on the process. However, comparison with the results of other authors demonstrated that butane pyrolysis proceeds in the same way in gold, pyrex and quartz reactors and the

reaction order with respect to butane is 1.5. From this, the authors infer a homogeneous character of the process. Oxygen, which was fed in a concentration of only 5–500 ppm, had a very pronounced effect on the pyrolysis. The supply of only 7 ppm of oxygen decreased the formation of hydrocarbon products of cracking by 70%, the general pattern of product distribution being retained. However, increased yields of butenes, butadiene and water were noted in this case.

The effect of small admixtures of oxygen (2%–3% with respect to propane) on the propane pyrolysis in a quartz flow reactor under atmospheric pressure and at temperatures of 600–750 °C was studied to elucidate the process mechanism. At low conversion (low temperature or small residence time), propylene was the major product. However, as the conversion increased, the yields of methane and ethylene increased, while the yield of water decreased (Fig. 10).

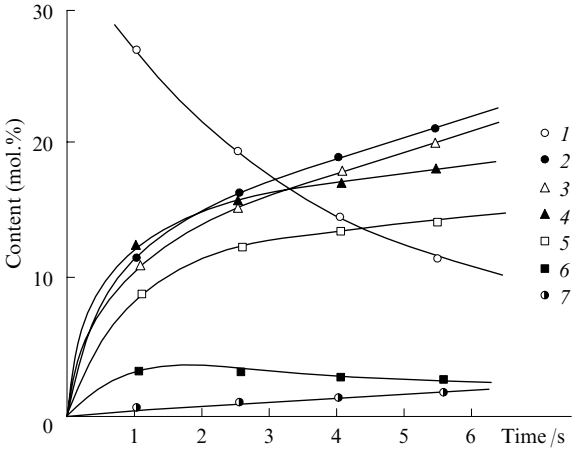


Figure 10. Propane conversion and product yields *vs.* time in the presence of 2% O_2 at 700 °C.[26]
(*1*) Propane (on 1/2 scale), (*2*) methane, (*3*) ethylene, (*4*) propylene, (*5*) hydrogen, (*6*) water, (*7*) ethane.

As the oxygen concentration increased from 2% to 3%, the propane conversion rate increased at any temperature (Fig. 11), so did the yields of other main products — propylene, methane, ethylene, ethane, hydrogen and water. The kinetic model proposed in the study cited, which comprises 28 steps, described adequately the obtained results.

The influence of minor oxygen admixtures on the pyrolysis of ethane and propane was studied in a continuous flow quartz reactor at 0.8 atm, a contact time of ~5 s and temperatures of 550–800 °C.[27] In the presence of ~1.3 mol.% of oxygen, ethane started to react at much lower temperature than in the pyrolysis of pure ethane (Table 2, Fig. 12). For example, a 10% conversion was attained at a ~75 degrees lower temperature (590 °C instead of 665 °C). As conversion increases, the temperature difference diminished. The presence of oxygen also affected the selectivity of product formation. The discrepancy between the kinetic modelling and the obtained results did not exceed 23 degrees.

An equal increase in the reactivity was observed also in the pyrolysis of propane (Fig. 13). However, in the case of

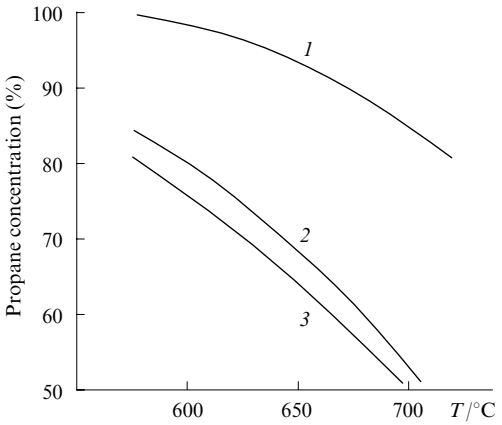


Figure 11. Effect of oxygen on the variation of propane concentration (reaction time 0.1 s).[26]
Concentration of O_2 (%): 0 (*1*), 2 (*2*), 3 (*3*).

Table 2. Temperature shift (ΔT) in ethane and propane pyrolysis in the presence of oxygen(~1.3 mol.%).[27]

Conversion	Ethane		Propane	
	ΔT_{exp}	$\Delta T_{mod}-\Delta T_{exp}$	ΔT_{exp}	$\Delta T_{mod}-\Delta T_{exp}$
0.10	77	−17	95	48
0.15	55	−23	73	47
0.20	39	−18	54	45
0.60	6	−2	5	5

propane, the kinetic modelling gave substantially underestimated results as compared with experimental data. Analysis of the sensitivity has shown that the results of modelling considerably depend on the rate constant for the reaction of the alkyl radicals with oxygen, which is much less reliable for propyl radicals than for ethyl radicals.

However, the effect of oxygen admixture on the process rate is rapidly mitigated as the number of the carbon atoms in the alkane molecule increases. The time periods needed to attain a 60% conversion in the pyrolysis and the partial oxidation (for alkane : O_2 = 1) differ by a factor of more

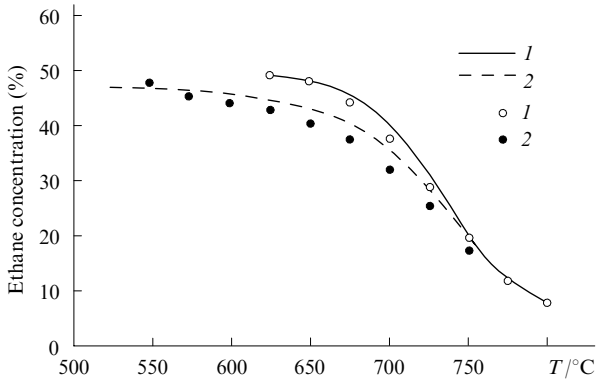


Figure 12. Experimental (dots) and calculated (lines) ethane conversions in the absence (*1*) and in the presence (*2*) of oxygen.[27]
Mixtures $C_2H_6 : N_2 = 49.6 : 50.7$ and $C_2H_6 : N_2 : O_2 = 50 : 48.6 : 1.3$.

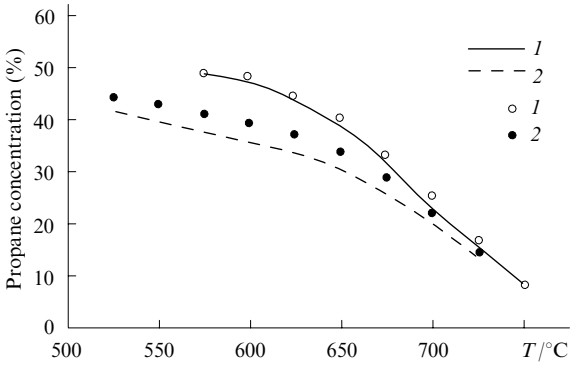


Figure 13. Experimental (dots) and calculated (lines) propane conversions in the absence (*1*) and in the presence (*2*) of oxygen.[27] Mixtures $C_3H_8 : N_2 = 49.6 : 50.7$ and $C_3H_8 : N_2 : O_2 = 50 : 48.6 : 1.3$.

than 15 for ethane, while for n-butane and isobutane this ratio is only ~ 3, and for n-hexane this is < 2 (see Ref. 28).

3. Catalytic oxidative pyrolysis of $C_2 - C_4$ alkanes

High yields of oxidative pyrolysis and oxidative dehydrogenation of light alkanes are achieved by using various catalytic systems. Formally, these works are beyond the scope of this review; however, the complex heterogeneous-homogeneous oxypyrolysis process and especially the temperature dependence of the product composition cannot be analyzed without considering the processes taking place on the surface of the catalyst, inert filling material and reactor internals. Meanwhile, as it was convincingly shown in recent publications,[29–32] the relatively high temperatures that are needed in some cases for the catalytic oxypyrolysis of light alkanes make intensive gas-phase steps inevitable; therefore, in the general case, these reactions must be treated as a single heterogeneous-homogeneous reaction. Hence, the review contains a section devoted to modern views on the mechanism of the catalytic dehydrogenation of $C_2 - C_4$ alkanes and on the interplay of heterogeneous and homogeneous steps of this process.[29–32]

All catalysts used for oxidative dehydrogenation and cracking of light alkanes can be conventionally divided into two large groups: those operating at relatively low temperature and those operating at high temperature. It is convenient to take a temperature of 450–500 °C as a conventional boundary. Below this boundary, the mixed V–Mo–Nb oxide catalysts first described by Thorsteinson *et al.*[33] are active. The authors of this pioneering study ascertained that catalysts of this group are fairly effective in the oxidative dehydrogenation of ethane. However, in the case of propane, their selectivity towards propylene is rather low, as they produce large amounts of carbon oxides and acetic acid upon successive destructive oxidation of propylene, most likely, at the double bond. No data about the heterogeneous-homogeneous process performed by catalysts of this group have been reported.

Vanadium oxide systems are also effective among the catalysts for higher-temperature oxidative dehydrogenation of light alkanes.[8] There is extensive literature on the effect of the support and its type and of modification of the active phase on the catalytic properties of vanadium catalysts. Usually, supported catalysts and catalysts modified with additives are more active and selective than bulk and/or non-modified catalysts.

The observed phenomenological features of the oxidative dehydrogenation of $C_3 - C_4$ alkanes in the presence of modified supported V–Sb oxide catalysts[29] attest to a substantial contribution of gas-phase reactions to the overall transformation. Apparently, the catalyst surface participates in not only chain termination reactions but also in the generation of free radicals. The latter can participate in both gas-phase and heterogeneous reactions, which can then give rise to the corresponding $C_3 - C_4$ alkene and also cracking and destructive oxidation products. The dehydrogenation to cracking product ratio is largely determined by the competition of reactions involving primary alkyl radicals and by the ratio of free reactor volume to the volume occupied by the catalyst. Vislovskiy *et al.*[29] showed experimentally that the oxidative dehydrogenation of propane and isobutane using catalysts of different composition is accompanied by an atypical effect of increasing degree of conversion following increase in the catalyst particle size. The authors attributed this finding to additional conversion of reactants upon homogeneous reactions taking place in the free gas volume between the catalyst particles. Although these reactions are initiated by the primary radicals formed in the heterogeneous reaction of the $[O]_{(s)}$ surface sites of the catalyst with the alkane

$$[O]_{(s)} + C_nH_{2n+2} \longrightarrow [OH]_{(s)} + C_nH^{\bullet}_{2n+1},$$

their efficiency increases as the contribution of the heterogeneous decay of charge carriers decreases and, hence, as the characteristic size of the gas gaps between the catalyst particles increases. The subsequent fate of these radicals depends on the relative contributions of the homogeneous and heterogeneous reactions in which they participate. For example, in the presence of a catalyst, the alkyl radical can rapidly react with another $[O]_{(s)}$ surface site to give an alkene molecule, which escapes to the gas phase.

$$[O]_{(s)} + C_nH^{\bullet}_{2n+1} \longrightarrow [OH]_{(s)} + C_nH_{2n}$$

And this results in higher selectivity of the formation of dehydrogenation products over cracking products.

In the gas-phase reactions, the intensive interaction of alkyl radicals with oxygen gives rise to alkyl peroxide radicals and then to oxygenate products, which are then oxidized to give mainly CO. In the presence of a catalyst, most of the arising radicals react on the catalyst surface to give mainly deep oxidation products. This leads to a sharp increase in the yield of CO_2 and, hence, decrease in the $CO : CO_2$ ratio.

The same publication[29] demonstrates that filling of the free reactor volume after the catalyst layer with an inert material, for example, fine quartz, induces a considerable shift from the cracked hydrocarbon products to hydrocarbon dehydrogenation and oxidation products. In this case, CO_2 rather than CO becomes the major carbon oxide product. All this attests to switching from predominantly homogeneous to predominantly heterogeneous transformation of active species in the packed space after the catalyst layer.

As the degree of filling of the reaction volume with the catalyst or inert material increases, the alkane conversion may decrease due to the decrease in the contribution of

homogeneous processes, although in the absence of the catalyst, homogeneous oxypyrolysis does not proceed by itself at this temperature. Although the contribution of homogeneous processes to the overall transformation may be rather high in the catalytic oxidation, the product distribution is controlled by the properties of the catalyst. It is noteworthy that these effects can be observed on catalysts and solids irrespective of their chemical composition or catalytic properties. This implies that any oxide surface not only terminates radical chain processes but also introduces certain changes in the chemistry of the process. Thus, in the oxidative dehydrogenation of light alkanes, the heterogeneous and homogeneous processes are inseparably interrelated.

Sinev *et al.*[30] showed that the oxidative dehydrogenation of C_2-C_4 alkanes in the presence of the same supported V–Sb oxide catalysts is accompanied by intensive hydrogen formation, the hydrogen yield being in some cases even higher than the yield of alkene. This was attributed, apart from the non-oxidative dehydrogenation of alkanes in the reactor volume after the catalyst layer (where the oxygen concentration is low), to the active role of gas-phase processes in the catalytic oxidation, due to which the heterogeneous formation of alkyl radicals is accompanied by gas-phase reactions

$$C_nH^{\cdot}_{2n+1} \longrightarrow H + C_nH_{2n}$$

$$C_nH_{2n+2} + H \longrightarrow C_nH^{\cdot}_{2n+1} + H_2,$$

and to the presence of an 'aldehyde' channel, which starts from the oxidation of the alkene at the double bond and includes a series of fast free-radical processes

$$RHC{=}CH_2 + R'O^{\cdot} \longrightarrow RCH_2C(O)H + R'^{\cdot}$$

$$RCH_2C(O)H \longrightarrow RCH^{\cdot}_2 + C(O)H^{\cdot}$$

$$C(O)H^{\cdot} \longrightarrow CO + H^{\cdot}$$

$$R''H + H^{\cdot} \longrightarrow R''^{\cdot} + H_2$$

Thus, the catalytic formation of each alkyl radical can give rise to a non-branched gas-phase chain reaction producing equal amounts of alkene and hydrogen. A higher yield of hydrogen compared to the alkene yield may be related to the occurrence of gas-phase oxidative reactions. In addition, with some catalysts, for example, $VO_x/\gamma\text{-}Al_2O_3$, this can be related to soot formation.

The effect of the nature and the surface density of the oxidation active sites $[O]_{(s)}$ on the distribution of products of the autothermal oxidative dehydrogenation of propane on non-reducible (Pt-containing or rare earth and alkaline earth metal oxide-based) and reducible (vanadium oxide-based) catalysts has been considered.[32] According to experimental data, the catalytic behaviours of these two types of catalysts are considerably different, first of all, they povide different $C_3H_6:C_2H_4$ ratios of the products. In the presence of first group catalysts, ethylene predominates. This implies that the surface properties of oxides that participate in alkane activation and in the transformation of the intermediate active species play important role for determination of the chemical transformation pathway.

If the primary propane activation gives the propyl radical, then in the absence of oxygen, the relative yields of ethylene and propylene are determined by the competition of cracking and hydrogen atom abstraction reactions:

$$C_3H^{\cdot}_7 \longrightarrow C_2H_4 + CH^{\cdot}_3$$

$$C_3H^{\cdot}_7 \longrightarrow C_3H_6 + H^{\cdot}$$

In accordance with the kinetic parameters of these reactions, both n-propyl and isopropyl radicals should be predominantly converted to propylene, and the $C_3H_6:C_2H_4$ ratio should increase with temperature.[32] The higher yield of ethylene *versus* propylene observed experimentally with rare earth and alkaline earth metal oxides was attributed by Kondratenko and Sinev[32] to higher rate of the subsequent processes of deep oxidation of propylene on these catalysts caused by the presence of a weakly bonded H atom in its CH_3 group. Even in the gas phase, in the temperature range of 550–650 °C, the abstraction of an H atom from propylene by an O_2 molecule occurs ~300–700 times faster than that from ethylene.

However, V-containing catalysts of oxidative dehydrogenation have high surface density of active sites with high affinity for H atoms. The H atoms can be detached from the $C_3H^{\cdot}_7$ radicals, in which the C–H bond is much weaker than this bond in propane (~35 and 95 kcal mol^{-1}, respectively), with a very low activation energy and, hence, at a very high rate to yield propylene. Thus, when the density of the oxidation sites on the catalyst surface is large enough, this heterogeneous reaction is much more effective than the gas-phase reactions of the $C_3H^{\cdot}_7$ radical. In this particular case, the $C_3H_6:C_2H_4$ ratio is to a much greater extent dictated by the active site concentration on the catalyst surface than by their activity. This is why V-containing catalysts produce higher $C_3H_6:C_2H_4$ ratios than non-reducible oxides.

Under steady-state conditions, the rate of oxidative dehydrogenation of propane in the presence of vanadium-containing catalysts can be mainly determined by the re-oxidation rate of reduced sites.[32] At high degree of conversion of oxygen (the limiting reagent in the oxidative dehydrogenation), the vanadium oxidation state in the alumina-supported catalysts may be low (V^{3+}). Therefore, additives that accelerate re-oxidation (*e.g.*, antimony) noticeably enhance the efficiency of V-containing catalysts of the oxidative dehydrogenation of light alkanes.

An additional factor to reduce the selectivity is the participation of the lattice oxygen of the vanadium-containing catalysts in the formation of carbon oxides, which was revealed in a study of propane oxidation.[32] Although the reduction of these catalysts by light alkanes entails continuous increase of the binding energy of the lattice oxygen and the corresponding decrease in its reactivity, the products of deep oxidation are formed in parallel with the oxidative dehydrogenation to almost complete reduction of vanadium to the V^{3+} state.[34] After that, alkenes continue to be formed in non-oxidative processes with simultaneous formation of hydrogen.[30, 32, 34]

A study of the catalytic oxidative dehydrogenation and cracking of C_3-C_4 alkanes catalyzed by manganese compounds promoted by sodium phosphate revealed[35] a competition of the oxidative dehydrogenation and the oxidative cracking of these hydrocarbons. At a contact time of > 1 s, the oxidative destruction starts to prevail over dehydrogenation, and this results in different time dependences of the ethylene and propylene yields (Figs 14 and 15). This allows the ethylene to propylene ratio in the products to be varied by varying the contact time as well as the content of the Na_3PO_4 promoter.

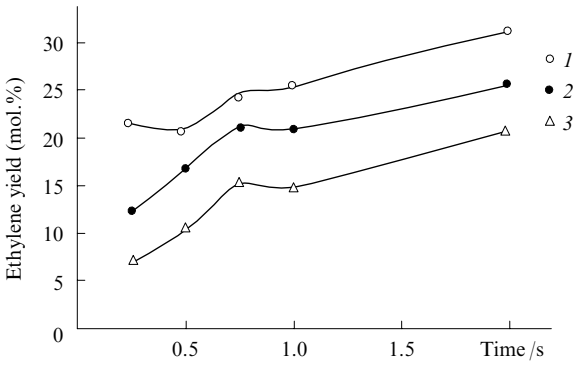


Figure 14. Ethylene yield in the propane oxidation *vs.* residence time on manganese catalysts at 730 °C at different contents of the promoter (Na_3PO_4): (*1*) 1%, (*2*) 5%, (*3*) 3%.[35]

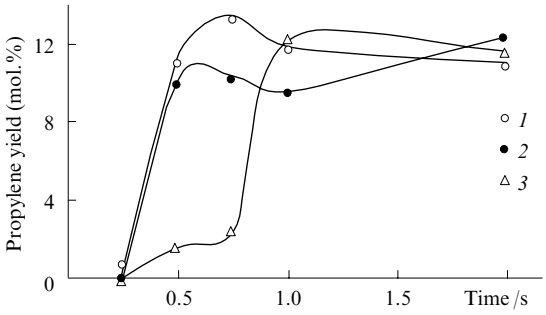


Figure 15. Propylene yield in the propane oxidation *vs.* residence time on manganese catalysts at 730 °C.[35]
Amount of the promoter (Na_3PO_4): (*1*) 5%, (*2*) 3%, (*4*) 1%.

For all of the manganese catalysts studied, temperature rise contributes to increase in the ethylene yield (Fig. 16).

The above brief analysis of the studies on the catalytic oxidative pyrolysis of light alkanes demonstrates that now there exist substantiated views on the mechanism of activation of the initial hydrocarbon and formation of the major products and on the role of heterogeneous and homogeneous factors in this process.

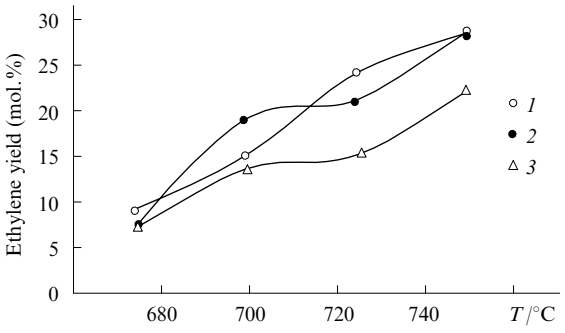


Figure 16. Ethylene yield in the propane oxidation on manganese catalysts *vs.* reaction temperature (residence time 0.75 s).[35]
Amount of the promoter (Na_3PO_4): (*1*) 1%, (*2*) 5%, (*3*) 3%.

4. Oxidative pyrolysis at short contact time with the catalyst

In recent years, studies of oxidative dehydrogenation and pyrolysis of light alkanes at short time ($\sim 1-10$ ms) contact of reactants with the catalyst being heated to high (800–1200 °C) temperature[36,37] at which gas-phase processes undoubtedly play important, if not the determining, role have become popular. Probably, selective oxidative dehydrogenation of ethane over millisecond contact times at atmospheric pressure and a temperature of 850–1000 °C was first studied by Huff and Schmidt.[38] The reaction proceeded in the autothermal mode by using its own heat. External heating of the catalyst was used only in the initial period to trigger the reaction. In the subsequent studies, Schmidt and co-workers demonstrated the possibility of obtaining high yields of alkenes upon short time contact with the monolithic catalyst based on Pt-coated Al_2O_3 in the oxidative dehydrogenation of propane,[39–41] n-butane and isobutane[39,42,43] and C_5 and C_6 alkanes.[44,45]

The selectivity of ethylene formation on a honeycomb-supported Pt catalyst in the autothermal mode at a $C_2H_6:O_2 \approx 1.7$ ratio and a pressure in the reactor of 1.4 atm reached 70% at ethane conversion of >80%.[38] The use of an Rh catalyst under similar conditions resulted in the predominant formation of synthesis gas, and the use of Pd led to carbon black formation. The authors attributed this difference to different mechanisms of purely catalytic oxidative dehydrogenation of ethane on these metals. In particular, they suggested that the Pt-catalyzed process starts as oxidative dehydrogenation, which is followed by elimination of β-hydrogen from the adsorbed ethyl radical with subsequent ethylene desorption.

Despite the high temperature in the reactor, early interpretation of these results was based on predominantly catalytic mechanism of formation of the major products.[42,46] It was considered that in the Pt- and Rh-catalyzed heterogeneous oxidation of methane, carbon [$C_{(s)}$] formed on the surface upon pyrolysis rapidly reacts with the surface oxygen [$O_{(s)}$] to give CO, which is rapidly desorbed. Hydrogen leaves the surface either as H_2 or as H_2O depending on the activation energy of formation of the $OH_{(s)}$ groups on the metal surface. Hydroxy groups are formed more easily on the Pt surface than on the Rh surface, which accounts for higher yield of H_2O and lower yield of H_2 on Pt than on Rh. In the Ni- or Rh-catalyzed oxidation of CH_4, no C_{2+} products were detected, while in the Pt-catalyzed reaction, the selectivity of formation of C_2H_4 and C_2H_6 reached 1%; in the case of Pd, this selectivity was somewhat higher but this catalyst was rapidly deactivated.

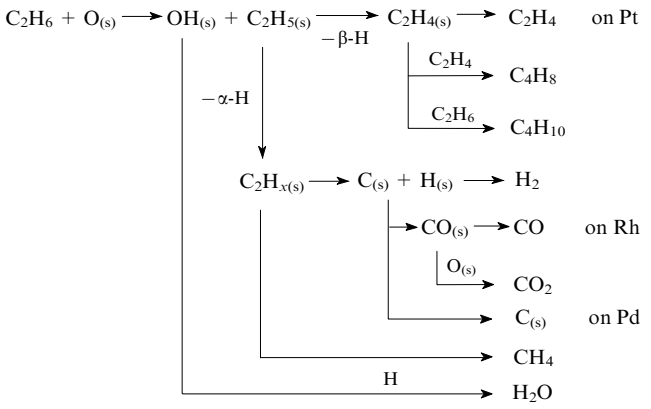
It was assumed[40] that ethane oxidation induced by heterogeneous activation

$$C_2H_6 + O_{(s)} \longrightarrow C_2H_{5(s)} + OH_{(s)}$$

involves one of the overall reactions shown in Scheme 1, depending on the catalyst used.

The 70% selectivity of ethylene formation observed on Pt was attributed[40] to the fact that β-hydrogen elimination predominates on this catalyst. Conversely, for Rh and Pd, fast elimination of both α- and β-hydrogen atoms was assumed, resulting in subsequent reactions to give synthesis gas or solid carbon. The more 'noble' the metal behaviour, the higher the tendency for hydrogen elimination particularly from the β-position. From this standpoint, the higher yield of ethylene on the Pt catalyst appears reasonable. It

Scheme 1



was noted that the Pd-catalyzed reaction gives, in an early period of time, synthesis gas and ethylene in amounts comparable with their amounts on Pt but after that, this catalyst is rapidly deactivated due to soot deposition.

Like oxidation of ethane, Rh-catalyzed oxidation of propane gives synthesis gas as the predominant product, and in the case of a Pt catalyst, ethylene is mainly formed. Since in this case, the C_2H_4 to CH_4 ratio reached 2 : 1, cracking was considered as the predominant mechanism. Depending on the way of subsequent adsorption of the propyl radical that forms (by either primary or secondary carbon atom), ethylene or propylene is produced. Since the probability of the former event is twice that of the latter, the ratio of the yields of these products ($Y_{C_2H_4}/Y_{C_3H_6}$) is expected to be ~ 2, which is in good agreement with the actual results. Meanwhile, in the case of Rh, once hydrocarbon has been adsorbed on the surface, the elimination of particularly β-hydrogen is not preferred, and this is in line with complete destruction of the adsorbed molecule and the observed subsequent desorption of CO and H_2. Nevertheless, the authors supposed that in such a heterogeneous-homogeneous system, cracking of C_3H_8 may also take place in the gas phase. In this case, ethylene and methane are products of endothermic cracking, while the role of oxygen is reduced to provision of the heat needed for cracking, which comes from exothermic catalytic reactions of deep or partial oxidation of some of the hydrocarbon. Similar conclusions were drawn for butane oxidation.

However, the results of publications[47–49] and some other works indicate that gas-phase reactions play a crucial role even in the catalytic processes, especially at temperatures above 600 °C, and a > 30% yield of ethylene can also be obtained without a catalyst. Morales and Lunsford[47] considered generation of alkyl radicals on the catalyst surface followed by their release to the gas phase to be a rather general phenomenon. In the case of ethane, the release of ethyl radicals to the bulk and their subsequent gas-phase reaction with O_2 afford C_2H_4. The formation of ethylene upon the oxidative dehydrogenation of ethane at 700–900 °C and millisecond contact times in the presence of Pt and Pt–Rh gauze catalysts was found[50] to occur in the gas phase. The role of the catalyst was only the efficient heat supply to the gas stream. Typically, in the presence of the Pt–Rh catalyst, the conversion of oxygen is not almost related to ethane conversion, whereas in an empty reactor and on the supported catalyst, they are converted simultaneously (Fig. 17). The researchers cited attributed this to

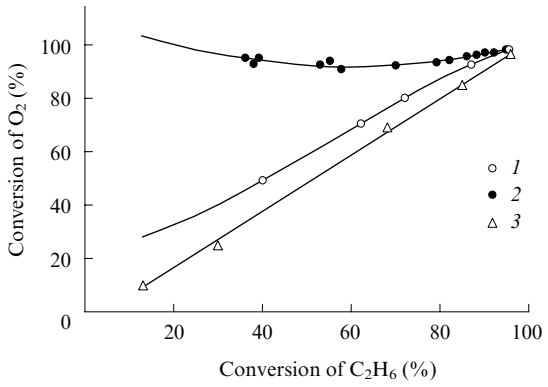


Figure 17. Conversion of O_2 *vs.* conversion of C_2H_6 in catalytic and non-catalytic processes.[50]
The ratio $C_2H_6 : O_2 = 1.7$; reactant flow rates (ml min^{-1}): C_2H_6, 268; O_2, 158; Ar, 1575. (*1*) Empty reactor, (*2*) Pt–Rh gauze, (*3*) monolithic catalyst.

considerably different thermal modes in a Pt gauze reactor as compared with an empty reactor or a supported catalyst. Due to the more efficient formation of deep oxidation products on a Pt gauze (or near the gauze), which results in intensive heat evolution upon consumption of most oxygen for the formation of these products, the peak temperature on the Pt gauze is almost 100 degrees higher, and this leads to considerable differences in the oxidation mechanism. The absence of direct relationship between the conversion of oxygen and the conversion of C_2–C_5 alkanes under similar conditions was also noted in another publication.[51]

A comparison of experimental results[44] on partial oxidation of n-pentane, n-hexane and cyclohexane on Pt-coated monolithic catalyst at high temperature and a contact time of 5 ms with kinetic modelling of the homogeneous reaction demonstrated that most of data are properly interpreted in terms of the gas-phase process. Only with a great excess of the hydrocarbon (hydrocarbon : oxygen ratio > 0.9) corresponding to adiabatic heating of the mixture below 850–900 °C, the yield of CO_2 was higher than the yield predicted by the homogeneous kinetic model, which was attributed to its formation on the catalyst.

It was shown[52–54] that the oxidation of propane at temperatures < 500 °C in the presence of the industrial catalyst Pt/γ-Al_2O_3 at a millisecond contact time is a purely catalytic process the rate of which is controlled by only phase transfer of reactants. However, above 500 °C, gas-phase pyrolysis with predominant formation of alkenes occurs rather rapidly. This is confirmed, in particular, by the fact that greater catalyst loading results in higher yields of CO_2, CO, H_2O and H_2, whereas the yields of propylene, ethylene and methane decrease. At 700 °C, both oxygen and propane are completely converted and the reaction stoichiometry changes from the ratio propane : oxygen = 1 : 5, which is characteristic of complete oxidation, to the ratio 1 : 1. The selectivity of the formation of propylene, which is missing at low temperature, reaches a maximum of 28%–30% at 625 °C and then decreases to 13% at 700 °C at complete conversion of propane (Fig. 18). Starting from 550 °C, ethylene is formed, the selectivity of ethylene formation at highest experimental temperatures reaches

40%. Full selectivity with respect to alkenes is 55% – 60% at a propane conversion of > 60%. Over the whole temperature range studied, the formation of ethylene is accompanied by the formation of methane.

Replacement of the heterogeneous mechanism of propane oxidation by the homogeneous mechanism with increase in temperature is also evidenced by the change in the temperature difference between the reactor walls and the hot spot of the catalyst where deep oxidation of propane takes place. At low reactor temperature, the hot spot temperature is almost 100 degrees higher than the temperature of the walls. However, as the reactor temperature increases and approaches the maximum temperature and the yield of alkenes increases, this difference disappears almost completely.

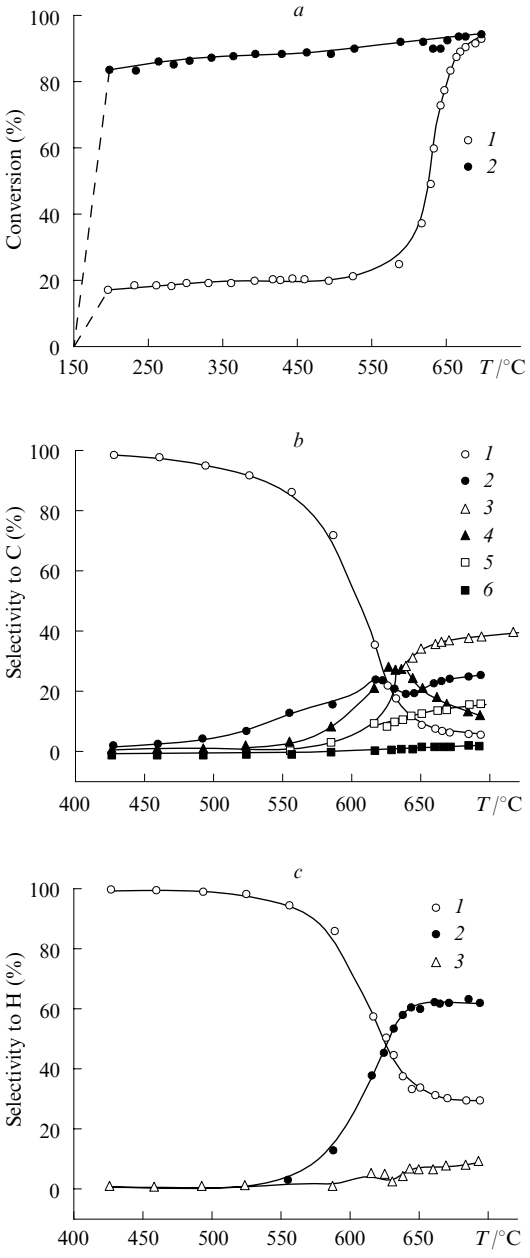


Figure 18. Propane oxidative dehydrogenation catalyzed by Pt/γ-Al_2O_3.[52]
Mixture composition $C_3H_8 : O_2 : N_2 = 1 : 1 : 4$; reactant flow rate 1.1×10^6 litre kg^{-1} (Cat.) h^{-1}.
(*a*) Conversion of propane (*1*) and O_2 (*2*); (*b*) selectivity to carbon: CO_2 (*1*), CO (*2*), ethylene (*3*), propylene (*4*), methane (*5*), ethane (*6*); (*c*) selectivity to hydrogen: H_2O (*1*), hydrocarbon sum (*2*), H_2 (*3*).

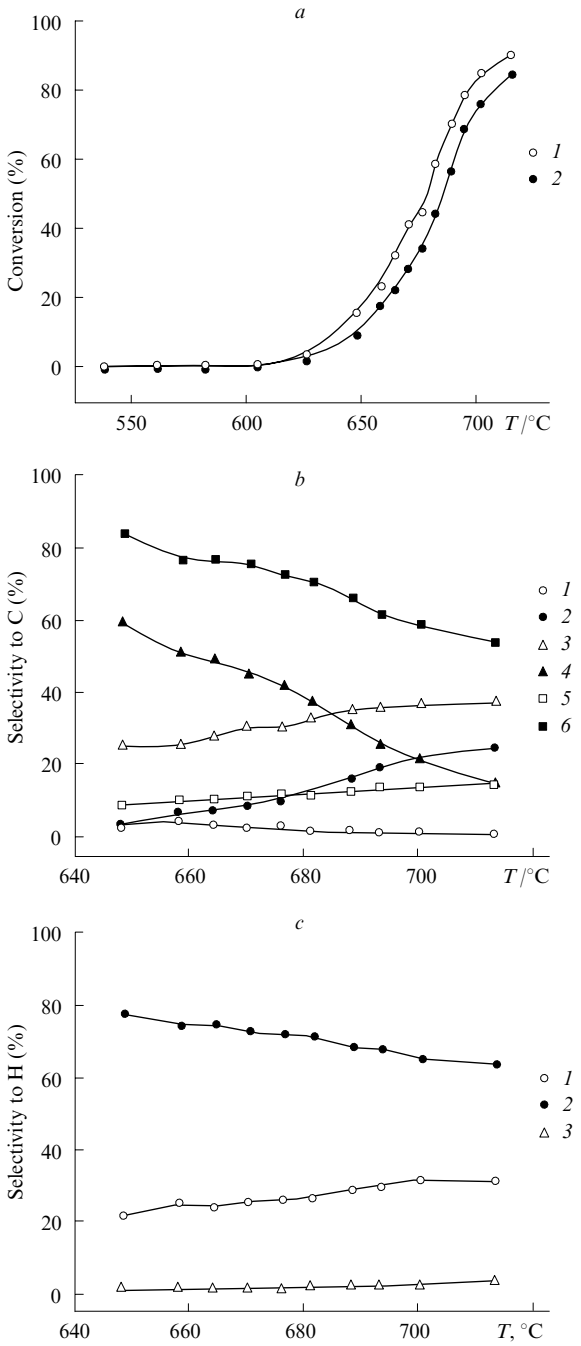


Figure 19. Effect of temperature on homogeneous oxidative dehydrogenation of propane.[52]
Mixture composition $C_3H_8 : O_2 : N_2 = 1 : 1 : 4$; reactant flow rate 130 cm^3 s^{-1}.
(*a*) Conversion of propane (*1*) and O_2 (*2*); (*b*) selectivity to carbon: CO_2 (*1*), CO (*2*), ethylene (*3*), propylene (*4*), methane (*5*), alkene sum (*6*); (*c*) selectivity to hydrogen: H_2O (*1*), hydrocarbon sum (*2*), H_2 (*3*).

The contributions of homogeneous and heterogeneous processes to the oxidative dehydrogenation of propane were compared by carrying out [53] a detailed study of the gas-phase process in an empty mullite reactor with a 7.3 cm^3 isothermal section at a flow rate of 0.1–1 m s^{-1} (see Ref. 52). The obtained temperature dependence (Fig. 19) corresponds to a 3.6 s contact time for room temperature and a ~1 s contact time for the highest temperature of the studied range.

The propane and oxygen conversion starts at 600 °C, and at 715 °C, the conversion of propane reaches 90%. At low temperature, propylene is the major alkene that is formed, but the selectivity of its formation decreases from 60% to 17% as the temperature increases. The selectivity of ethylene formation increases to 40% but this does not make up for the overall decrease in the selectivity of alkene formation with temperature rise.

It follows from analysis of the kinetic model [9] that propylene and ethylene are formed upon elimination of the β-hydrogen atom or the CH_3 group from propyl radicals, whereas CO_x are the final products. Therefore, the selectivity of formation of alkenes is expected to increase following the decrease in the contact time.

The influence of the contact time was studied under variable flow rates of reactants in the range of 27–470 $cm^3\,s^{-1}$ (contact time variation from 0.175 to 3 s) at 686 °C (Fig. 20). The conversion of propane reaches nearly a steady-state level of 80%–85% when the time is 1.3 s and does not increase any longer at complete conversion of oxygen, since the reactor temperature is insufficient for activating the thermal pyrolysis of propane, as was shown by special experiments. At short contact times, propylene is the major product but then the selectivity of its formation decreases to 20%. The selectivity of ethylene formation somewhat increases with time (from 30% to 35%). However, the overall selectivity of alkene formation is >55% even at the highest conversion.

Nitrogen dilution of a propane–oxygen mixture results in a decrease in the conversion of both oxygen and propane. The ratio of the products almost does not change. Comparison of the oxidative dehydrogenation with pyrolysis in the absence of oxygen shows a sharp decrease in the conversion in the absence of O_2: it does not exceed 30% even at 740 °C. Whereas the major products of oxidative dehydrogenation are propylene and hydrogen, the major products of pyrolysis are ethylene and methane. The overall selectivity of alkene formation in the pyrolysis is high (up to 80%).

An interesting series of experiments was performed [52] for direct comparison of the oxidative dehydrogenation of propane in an empty reactor and in a reactor containing various amounts of the Pt/γ-Al_2O_3 catalyst in mixtures with various $C_3H_8:O_2$ ratios (1 : 1, 1 : 0.25 and 1 : 0) diluted with nitrogen approximately 12-fold (propane concentration is ~3.8%). For the ratio $C_3H_8:O_2 = 1:1$, the gas-phase conversion of propane starts at 650 °C and rapidly increases with temperature (Fig. 21). In the presence of the catalyst, a noticeable conversion of propane occurs over the whole range studied, but up to 650 °C it barely depends on temperature, and then rapidly increases, as in the gas-phase process.

In the absence of a catalyst, almost no CO_2 is formed, but in the presence of a catalyst, it forms in large amounts (Fig. 22). The carbon dioxide yield in the catalytic reaction is nearly constant up to the temperature where the gas-phase reaction starts, and then declines. Apart from CO_2, the major products of the catalytic reaction are H_2O, CO and H_2, their yields in the gas-phase reaction being also rather low, but they increase with increase in the catalyst volume. The fast increase in the yields of CO and H_2 with temperature acompanied by observable decrease in the CO_2 and H_2O, concentrations is probably attributable to the onset of catalytic partial oxidation and steam (or dry) reforming.

Conversely, the propylene yield diminishes as the catalyst volume increases, the yield being maximum in an empty reactor. The same is true for ethylene and methane (Fig. 23). No evidence supporting any noticeable contribu-

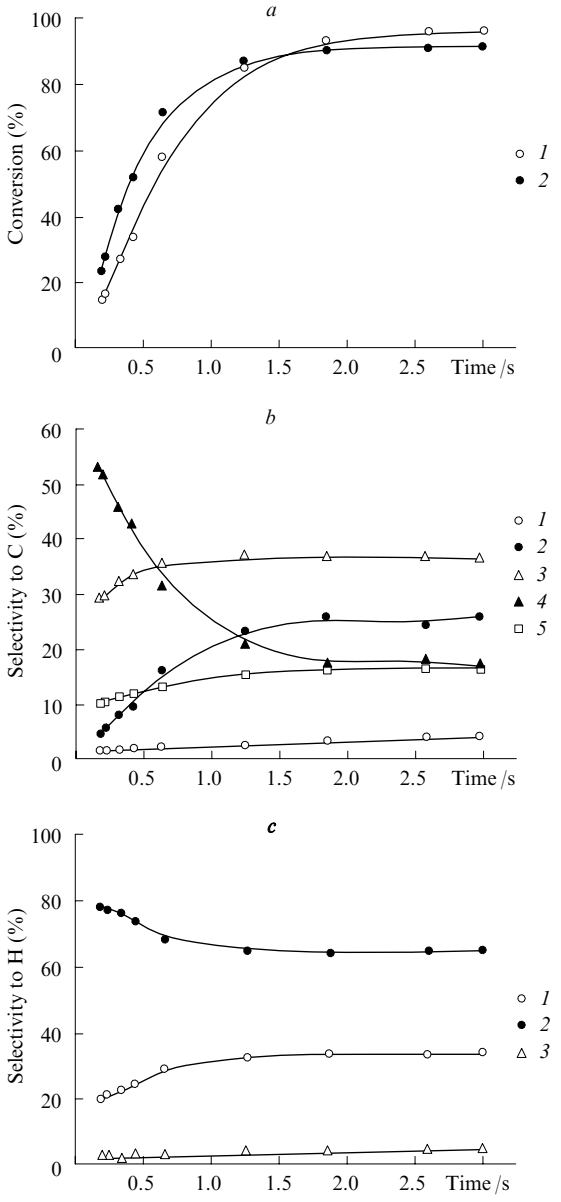


Figure 20. Effect of contact time on the homogeneous oxidative dehydrogenation of propane.[52]
Mixture composition $C_3H_8:O_2:N_2 = 1:1:4$; T = 686 °C.
(*a*) Conversion of propane (*1*) and O_2 (*2*); (*b*) selectivity to carbon: CO_2 (*1*), CO (*2*), ethylene (*3*), propylene (*4*), methane (*5*); (*c*) selectivity to hydrogen: H_2O (*1*), hydrocarbon sum (*2*), H_2 (*3*).

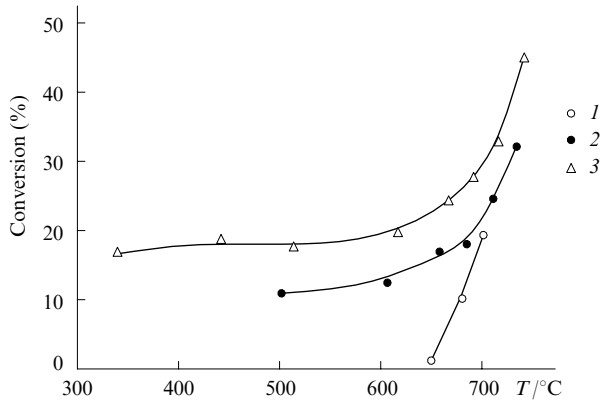


Figure 21. Conversion of propane in an empty reactor (*1*) and in the presence of the Pt/γ-Al_2O_3 catalyst for bed length of 1.5 cm (*2*) and 5 cm (*3*).[52]
Flow rates of C_3H_8 and O_2: 22 cm^3 min^{-1}; total gas flow rate (N_2 dilution): 578 cm^3 min^{-1}.

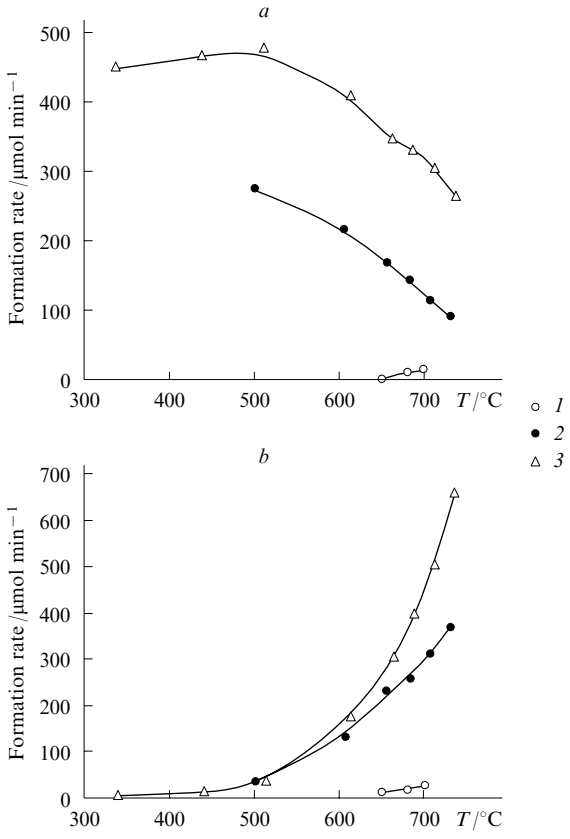


Figure 22. Temperature dependences of the CO_2 (*a*) and CO (*b*) formation rates in the oxidative dehydrogenation of propane in an empty reactor (*1*) and in the presence of the Pt/γ-Al_2O_3 catalyst for bed length of 1.5 (*2*) and 5 cm (*3*).[52]
Flow rates of C_3H_8 and O_2: 22 cm^3 min^{-1}; total gas flow rate (N_2 dilution): 578 cm^3 min^{-1}.

tion of the catalytic process to the formation of alkenes was found in these experiments. Moreover, the active role of the catalyst in oxidative processes results in partial conversion

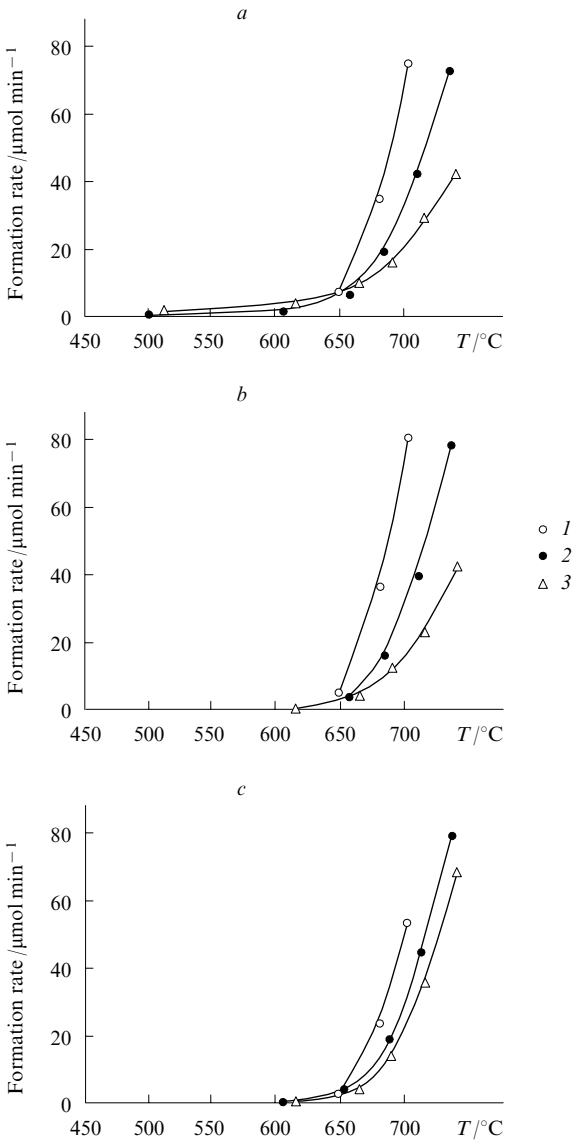


Figure 23. Formation rates of C_3H_6 (*a*), C_2H_4 (*b*) and CH_4 (*c*) *vs.* temperature in the oxidative dehydrogenation of propane in an empty reactor (*1*) and in the presence of the Pt/γ-Al_2O_3 catalyst for bed length of 1.5 (*2*) and 5 cm (*3*).[52]
Flow rates of C_3H_8 and O_2: 22 cm^3 min^{-1}; total gas flow rate (N_2 dilution): 578 cm^3 min^{-1}.

of the formed propylene, ethylene and methane when oxygen is present.

The decrease in the oxygen supply down to $C_3H_8 : O_2 = 4$ leads to corresponding decrease in the propane conversion in the catalytic reaction region and less pronounced dependence of the conversion on the catalyst volume. Simultaneously, the yields of CO_2, H_2O, CO and H_2 considerably decrease but still depend on the catalyst loading, thus pointing to the heterogeneous formation mechanism of these products. The propylene, ethylene and methane yields somewhat decrease under the homogeneous reaction conditions with reduced oxygen content. The addition of a Pt catalyst decreases the yields of these products, although to a lesser extent than at higher oxygen

content, probably, due to lower rate of their non-selective catalytic conversion to deeper oxidation products.

Experiments without oxygen supply to the reactor corresponding to thermal pyrolysis showed that the temperature dependence of propane conversion is almost the same in empty reactor and in the presence of various catalyst volumes. In all cases, four major products formed, namely, propylene, hydrogen, ethylene and methane. The product yields were not noticeably affected by the presence of a Pt catalyst. Thus, although Pt catalysts are widely used in industrial dehydrogenation processes, under the given conditions in the absence of oxygen, only homogeneous thermal dehydrogenation of propane to propylene and hydrogen and thermal cracking of propane to ethylene and methane take place, which fully accounts for the observed product yields. This may be due to higher reactant flow rates in this study [10^6-10^7 litre kg^{-1} (Cat.) h^{-1}] compared with flow rates used in industrial processes [10^2-10^4 litre kg^{-1} (Cat.) h^{-1}] performed by the same catalysts.

Thus, unlike the interpretation proposed by Schmidt and co-workers, the authors of the study cited [52] did not find any evidence in favour of heterogeneous formation of alkenes. Currently most researchers are inclined to this interpretation according to which the main role of the catalyst is to supply heat of the catalytic reaction for the subsequent gas-phase endothermic dehydrogenation. The heat comes from catalyzed oxidation of some of propane to CO, CO_2 and H_2O.

According to kinetic modelling data,[53] the difference between the gas-phase pyrolysis and oxidative dehydrogenation of propane is first of all in the active role of the radicals $OH^{\bullet}$, which are formed in the presence of oxygen and which react with alkanes at a higher rate than the alkyl radicals $R^{\bullet}$ do. As a result, propane conversion occurs markedly faster (Fig. 24).

The difference between the selectivities of product formation in these processes (Table 3) is not very large. The

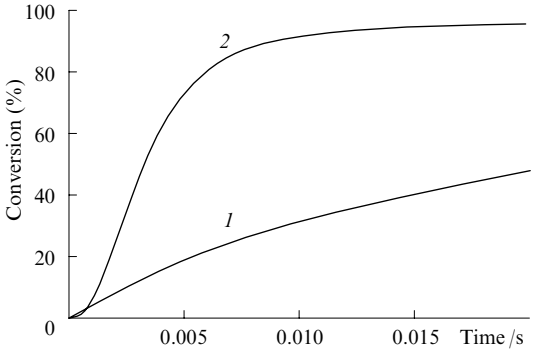


Figure 24. Calculated propane conversion *vs.* time for gas-phase pyrolysis (*1*) and oxidative dehydrogenation (oxidative pyrolysis) (*2*).[53]
$C_3H_8:O_2 = 1:1$, 900 °C, $p = 1$ atm.

oxidative dehydrogenation of propane provides lower selectivity towards methane than pyrolysis, because in this case, the methyl radical can not only be converted to methane but also react with oxygen to finally give oxygenates, mainly formaldehyde, the subsequent reactions of which give CO and CO_2 (see Table 3). Raising the temperature from 800 to

Table 3. Comparison of the calculated product distributions [a] for the oxidative and thermal pyrolysis for propane conversion of 50% ($C_3H_8:O_2 = 1:1$, $T = 900$ °C, $p = 1$ atm).[53]

Products	Oxidative pyrolysis	Pyrolysis
CH_4	33.1	52.2
C_2H_2	1.0	1.8
C_2H_4	54.2	55.5
C_2H_6	4.6	2.2
C_3H_4	0.7	0.3
C_3H_6	27.8	37.9
C_4H_6	0.2	0.7
C_4H_8 (see [b])	1.4	1.6
C_5	0.3	0.5
Acrolein and acetone	1.0	
CH_3CHO [c]	4.7	
CH_3OH	2.2	
CH_2O	13.3	
CO	21.7	
CO_2	2.4	

[a] Calculated as the number of moles of the product per mole of the consumed propane; [b] including 0.17% of C_4H_{10}; [c] including 1.7% of ketene.

1000 °C increases the conversion rate but affects little the product distribution.

Calculations show that in the autothermal mode and under more drastic conditions (lower $C_3H_8:O_2$ ratio), the yield of alkenes decreases but it is not clear whether this is due to higher temperature or kinetic effects.

The primary role of gas-phase reactions in the oxidative dehydrogenation of ethane and propane at temperatures above 600 °C was confirmed by investigation and kinetic modelling of this process.[55] In this process, ethane is highly selectively converted to ethylene, whereas CO and CO_2 are formed as by-products. At 650 °C and ~2 s reaction time, the gas-phase conversions of ethane and oxygen in their equimolar mixture were 80% and 90%, respectively, and the ethylene yield was as high as 56%. The propane conversion reached 80% at 675 °C. The conversion of oxygen was lower. The alkenes formed comprised propylene and ethylene (yields of up to 16% and up to 33%, respectively). Whereas the ethylene yield steadily increases with temperature, the propylene yield has a maximum, which indicates that on temperature rise, propylene is involved in secondary reactions. Pyrolysis gives also considerable amounts of methane, and above 650 °C, up to 20% of CO is formed. Kinetic modelling described well the experimental results. In particular, it was confirmed that the main effect of oxygen addition (aside from providing the autothermal mode) is activation of the process by accelerating the radical generation steps

$$C_2H_6 + O_2 \longrightarrow C_2H_5^{\bullet} + HO_2^{\bullet}$$

$$C_3H_8 + O_2 \longrightarrow C_3H_7^{\bullet} + HO_2^{\bullet}$$

The possibility of oxidative dehydrogenation in catalytic reactors with very short contact time demonstrated by Huff and Schmidt [38] aroused considerable interest and, hence, gave rise to a stream of new publications. In the presence of a Pt–Sn catalyst supported on a porous alumina, a selectivity towards ethylene of up to ~70% was attained, ethane

Table 4. Comparison of the partial oxidation of ethane to ethylene at millisecond catalyst contact times with ethane pyrolysis.[56]

Process (catalyst)	Feed /moles				Selectivity towards C_2H_4 (%)	Conversion of C_2H_6 (%)	Time /s
	C_2H_6	O_2	H_2	H_2O			
Pyrolysis	2	0	0	2	85	60	0.1
Partial oxidation (Pt)	2	1	0	0	64	69	10^{-3}
Partial oxidation (Pt – Sn)	2	1	2	0	83	73	10^{-3}

conversion being 70% and oxygen conversion being >99%.[56, 57]

It was found that admixing of hydrogen into the feed gas flow increases the selectivity of alkene formation up to >85%. This is due to the fact that hydrogen, which is oxidized more readily than ethane, functions as a sacrificial fuel, *i.e.*, its oxidation provides the heat needed to maintain the autothermal process. The function of the catalyst in this system is apparently to promote the oxidation of H_2 to H_2O. Simultaneously the ethane and ethylene oxidation and, hence, the formation of CO and CO_2 sharply decrease. Thus, the occurrence of endothermic dehydrogenation of C_2H_6 at the expense of the heat from hydrogen oxidation provides a high selectivity towards ethylene. Hydrogen is added to the ratio $H_2:O_2 = 2:1$; this ensures the most pronounced heating of the mixture and, moreover, this can be done using hydrogen that has been formed upon dehydrogenation.

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

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

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

Generally, this process is exothermic, as it finally gives more hydrogen than it is necessary to ensure autothermicity, and additional fuel is required. The catalyst ensures selective oxidation of hydrogen, whereas pyrolysis of ethane takes place in the gas phase, *i.e.*, this is a typical homogeneous-heterogeneous process. An equally high selectivity for the same ethane conversion is achieved by very fast external heating of ethane.

Detailed mechanism of the process is still discussed; however, it was noted [56, 57] that the time needed to reach the observed ethane conversion is shorter than the time needed to reach an equal conversion in the homogeneous pyrolysis at the gas temperature being attained. Hence, it was suggested that ethane dehydrogenation occurs both in the gas phase and on the catalyst surface. However, it is more likely that high conversion over short contact time is due to the considerable release of reactive radicals generated on the catalyst surface to the gas phase.

This process design has lots of advantages. From the environmental standpoint, the use of hydrogen oxidation instead of hydrocarbon oxidation as the heat source reduces the greenhouse gas formation. The use of pure oxygen reduces the formation of NO_x. The reactor is much smaller and simpler than usual pyrolysis furnaces, and owing to the higher temperature, the selectivity reaches 85% at an ethane conversion of 70%. Comparison of this method of ethane to ethylene partial oxidation with the pyrolysis of ethane is depicted in Table 4.

As a modification of the homogeneous-heterogeneous process, a purely homogeneous system was proposed in which ethane was injected directly into the diffusion flame of a hydrogen burner.[6] This eliminates catalyst poisoning problems and enhances the process safety, as a hydrogen diffusion flame can be generated using a common burner with separate hydrogen, ethane and oxygen supply. The process temperature can be lowered to a value that is optimal for ethane pyrolysis by simultaneous steam injection into the system. According to theoretical estimates, high selectivity of ethylene formation (>85%) can be attained in this case at ethane conversion of >70%. The potential advantages of this process (Fig. 25) are, most of all, high efficiency of heat transfer and the absence of feedstock waste for the production of carbon oxides.

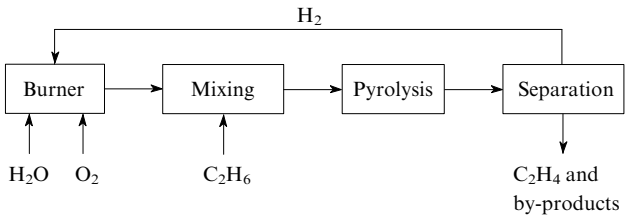


Figure 25. Block diagram of the homogeneous oxidative dehydrogenation of ethane.[6]

Numerous papers describing the application of this procedure and various catalysts (Pt – Sn, Pt – Rh, *etc.*) have lately been reported.[8] Instead of H_2, carbon monoxide or synthesis gas has also been added to the feed as sacrificial fuels.

According to the views formed in recent works, the catalyzed ethylene formation occurs in two steps. First, some of ethane (or the sacrificial fuel added) is oxidized on the catalyst to CO and H_2 or CO_2 and H_2O, and only after that, non-catalytic gas-phase thermal cracking of the remaining ethane to give ethylene takes place.

The catalysts for oxidative dehydrogenation of ethane optimal for short time catalysis in this type of process have been studied.[8] Monolithic cordierite substrates coated by γ-Al_2O_3 with Pt – Sn and $LaMnO_3$ catalysts deposited on the surface were used. It was found that gas-phase reactions indeed play an important role in this system. At temperatures of >800 °C, the results obtained in the absence of a catalyst are even superior to those obtained using Pt – Sn/Al_2O_3: a higher ethane conversion, although at a lower selectivity, is attained. In all experiments, both with and without the catalyst, the main by-products include CO, CO_2, H_2, H_2O and CH_4. In all experiments, acetylene was also detected, the selectivity of its formation being up to 4.8% at nearly complete ethane conversion (at $T = 900$ °C,

$C_2H_6 : O_2 : H_2 = 2 : 1 : 2$). Also, $C_3 - C_5$ hydrocarbons were found.

As expected, the conversion of oxygen was higher in the presence of $Pt - Sn/Al_2O_3$ than without a catalyst. Nevertheless, under no circumstances, the conversion of oxygen was complete and it never exceeded 96%. The author assumed that not all gas comes in contact with the catalyst but some of the gas passes by. In addition, it was found that neither cordierite nor alumina can be considered to be inert surfaces. The selectivity of ethylene formation on α-Al_2O_3 was higher than on γ-Al_2O_3 but lower than on cordierite. The presence of hydrogen considerably increased the selectivity of ethylene formation, diminished the formation of CO and increased the yield of water.

The results of this work leave no doubt that gas-phase reactions are highly important in the system in question, as they provide the greater part of ethylene. However, according to experiments, the catalyst also makes a direct or indirect contribution to the formation of ethylene.

A comparison of the two catalysts showed that at any temperature from 600 to 900 °C and the ratio $C_2H_6 : O_2 : H_2 = 4 : 1 : 2$, they provide almost equal conversions but the selectivity of ethylene formation is much higher on $Pt - Sn/Al_2O_3$. The catalyst $LaMnO_3$ was more active in the formation of complete conversion products and produced a higher yield of CO_2. Thus, the Pt – Sn catalyst is more effective for the oxidation of H_2 than $LaMnO_3$, which is more suitable for deep oxidation of hydrocarbons even in the presence of a substantial concentration of hydrogen. Comparison of three types of catalysts in this system is shown in Fig. 26.

The oxycracking of heavier hydrocarbons was also studied at short time contact with the catalyst.[40, 59] Whereas ethane decomposes to give ethylene, methane and CO, propane, n-butane, n-pentane and hexane are mainly cracked to afford propylene and ethylene (and also methane and CO_x) rather than undergo dehydrogenation. However, generally the yield of alkenes is low. In these experiments, the catalyst initiates the formation of alkyl radicals, which are then converted to alkenes in the gas phase.

A process and economic analysis of the industrial oxycracking of ethane and propane at short time (millisecond) contact with the catalyst was performed by Shell.[60] The experiments were carried out in a quartz reactor with an inner diameter of 11 mm and a length of 150 mm loaded with a supported metallic catalyst and operating in the autothermal mode at temperatures of 950 – 1100 °C and a pressure of 2.5 bar. The free reactor volume after the catalyst layer was ~8 ml. The reactor was fed with a well-stirred hydrocarbon and oxygen mixture (molar ratio $O_2 : C_n < 0.8$) at a linear velocity of 4 – 12 cm s^{-1}. Usually ethane served as the hydrocarbon feed, although experiments were also carried out with methane, isobutylene, propylene and butylenes. A typical residence time of reactants in the catalyst zone was 5 – 15 ms and that in the unfilled space after the catalyst layer was 150 – 500 ms. The reaction was triggered by heating the catalyst with a 150 W infrared lamp.

In these experiments, ethylene and CO_x were the major products of ethane conversion. The highest yield of ethylene (47%) was obtained on the Pt-based catalyst at the ratio $O_2 : C_n = 0.6 - 0.7$. Note that although the ethylene yield substantially depended on the type of catalyst and the $O_2 : C_n$ ratio, the selectivity of ethylene formation was

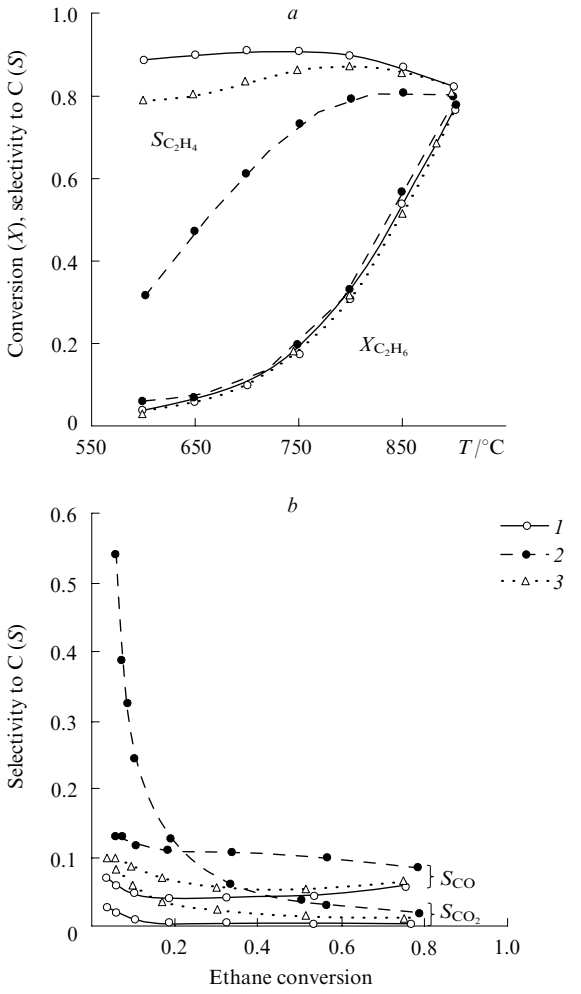


Figure 26. Temperature dependences (*a*) and relationship (*b*) of ethane conversion (X) and product selectivity (S) for three types of catalysts: 1% Pt – 2% Sn (*1*), $LaMnO_3$ (*2*) and 1% Pt – 2% Sn – $LaMnO_3$ (*3*).[58] $C_2H_6 : O_2 : H_2 = 4 : 1 : 2$.

strictly correlated with the ethane conversion. The decrease in the selectivity of ethylene formation upon increase in the ethane conversion is balanced by increased selectivity of methane formation (Fig. 27). Along with these products, acetylene (0% – 12%) and C_{3+} hydrocarbons (2% – 10%) were also detected.

Considering these results, the authors conclude that ethylene is formed in two steps under these conditions. First, some of the initial gas is oxidized in exothermic reaction to either CO and H_2 or CO_2 and H_2O, and this is followed by the endothermic thermal cracking of the remaining ethane to ethylene. The role of the catalyst is, apparently, reduced to initiation of the exothermic oxidation and to governing the amount of heat evolved depending on the selectivity ratio of deep (to CO_2 and H_2O) and partial (to CO and H_2) oxidation processes. The latter comprises also the accompanying water-gas shift and steam reforming reactions. The catalyst is likely to have no significant influence on the subsequent cracking.

Water injection suppresses the cracking of ethane, thus decreasing the yield of ethylene, due to heat absorption for water evaporation and steam reforming reaction. From

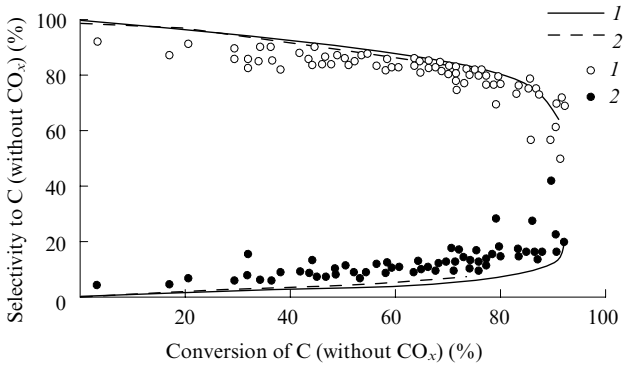


Figure 27. Selectivity of ethylene (*1*) and methane (*2*) formation *vs.* ethane conversion catalyzed by various Pt catalysts.[60]
Lines: calculated for $p = 2$ bar and $T = 900$ (*1*) and 850 °C (*2*).

experiments with pressure increase from 2 to 4 bar, it was inferred that the pressure has no marked influence on the catalytic combustion but decreases the selectivity of cracking to ethylene. However, analysis of the potential cost advantage that could be provided by commercialization of this process, based on the obtained results, showed that it would be only 2% – 3% relative to the cost of commercial implementation of traditional pyrolysis. This is too low to justify the expenditures for the development of new industrial process and commercialization risk. The saving of capital investment due to the oxycracking reactor, which is smaller and cheaper than the pyrolysis furnace, would be largely absorbed by the construction of air separation plant.[60]

Among the latest works on the preparation of alkenes by the catalyzed partial oxidation of ethane and propane, note the study[61] which reports a total ethylene and acetylene yield of >68% upon short time catalysis of Pt-doped $LaMnO_3$ at a selectivity of >80%.

Generally, numerous experimental results and the results of computer modelling in term of homogeneous kinetics lead to a quite definite conclusion about the general character of short time catalysis of the partial oxidation of light alkanes. On short time contact with the catalyst, some of the alkanes undergo deep oxidation to give CO_2 and H_2O with considerable heat evolution. Conversion of the rest of alkanes occurs at high temperature under homogeneous conditions, and this determines the composition of products.

5. Comparison of heterogeneous and homogeneous oxypyrolysis of $C_2 - C_4$ alkanes

A large number of catalytic systems were reported to be active in oxypyrolysis at temperatures from 350 to ~1000 °C.[62] However, almost all works noted that the active gas-phase process takes place above 600 °C. Under optimal conditions, the non-catalytic dehydrogenation of ethane was so efficient that at 600 °C and ethane : air = 1 : 2, the conversion of ethane reached 45%, the selectivity of ethylene formation being 73.7% and ethylene yield being 33%.[48] The authors specially noted that none of the catalysts they studied provided such a high yield under comparable conditions. A similar conclusion was made by the same authors as regards propane dehydrogenation: the selectivity of propylene formation in the catalytic reactions never exceeded the values obtained at the same propane conversion in the absence of a catalyst.[49]

Lemonidou and Stambouli[63] compared pyrolysis and oxydehydrogenation of n-butane and found that under optimized conditions, the non-catalytic reaction can be very effective and selective. At 580 °C and a residence time of 1.8 s, the conversion of n-butane reached 90% and the total selectivity towards $C_2 - C_4$ alkenes exceeded 55%. Considering the experimental results, the authors concluded that the role of oxygen in the mechanism of butane conversion is not limited to the radical initiation step, oxygen participating in chain propagation steps.

Among more recent publications, note the comparison[64] of ethane thermal cracking and oxidative conversion of ethane to ethylene under the following conditions: 600 – 850 °C, $O_2 : C_2H_6 = 0 - 0.2$; $H_2O : C_2H_6 = 0 - 3.3$; reactant gas hour space velocity (GHSV) 2 000 – 11 000 h^{-1}. The introduction of a minor amount of oxygen for the non-catalytic oxycracking of ethane increases not only the total conversion of ethane but also its conversion *via* purely thermal cracking. Simultaneously, the time needed to reach the same conversion upon thermal cracking decreases. Since the oxidative and thermal cracking occur in parallel under these conditions, the thermal efficiency of the process sharply increases and the demand for external energy supply considerably decreases. By selecting the process conditions, first of all, the temperature and the $O_2 : C_2H_6$ ratio, the process can be made exothermic. Furthermore, with oxygen added to reaction gases, no soot or resinous products were formed. Figure 28 shows the dependences of the reactant conversion and the selectivity of formation of the major products on the temperature and the $O_2 : C_2H_6$ ratio. It was noted that the presence of the metallic alloy Inconel 800 did not noticeably affect the selectivity of formation of ethylene and heavier alkenes and the formation of soot.

A detailed comparison of the thermal and oxidative pyrolysis of ethane under conditions as close as possible to industrial conditions [contact time 0.1 – 0.4 s, temperature 1173 K, pressure 1.4 atm, the ratio steam : ethane = 0.3 kg (H_2O) kg^{-1} (C_2H_6)] was reported.[65] In this study, 265 mm long heated tubular reactors made of sintered dense α-Al_2O_3 (corundum) or stainless steel (Incoloy 800) with an internal diameter of 8.0 mm were used. As the contact time increased, the ethane conversion and the yields of ethylene and most of other products increased to reach a plateau at times of >0.2 s. However, due to the increase in the yield of CH_4 following the increase in the contact time, the selectivity of ethylene formation became lower. Therefore, a time of 0.2 s was chosen. The conversion of oxygen was complete in all experiments.

Steam dilution [0.2 – 0.5 kg (H_2O) kg^{-1} (ethane)] had little influence on the results; therefore in experiments, the steam ratio was taken to be 0.3, which is usual for industrial units. Both the ethane conversion and the ethylene yield increased with temperature (Fig. 29). Higher temperatures led to considerable increase in the yields of methane and acetylene and to less pronounced increase in the carbon monoxide and propylene yields. The yield of propane slightly decreased. Since above 1173 K the selectivity of ethylene formation markedly decreases, this temperature is regarded as optimal.

An increase in the oxygen concentration entails an increase in the ethane conversion and only a minor decrease

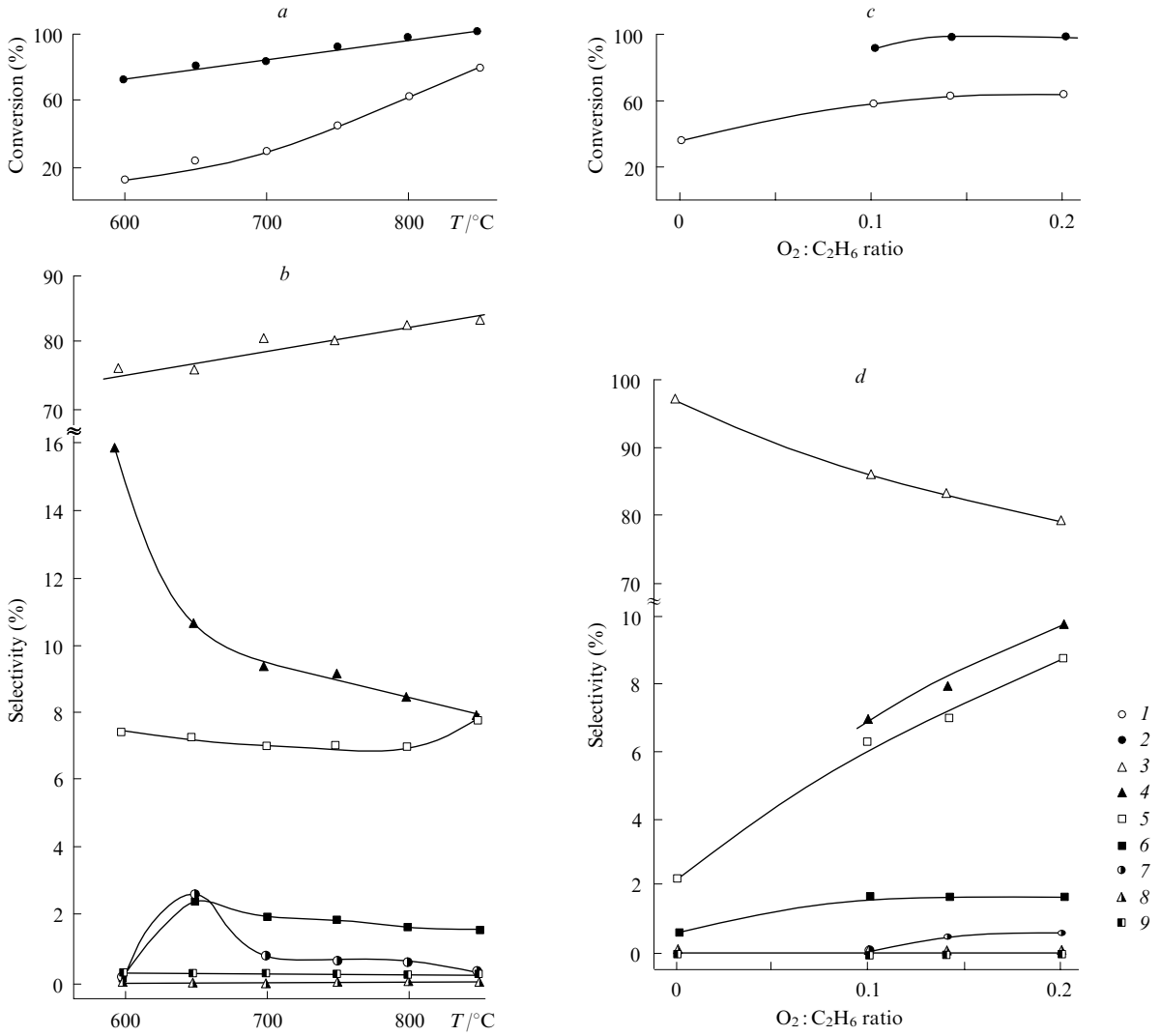


Figure 28. Conversion of reactants (ethane and O_2) and selectivity towards major products *vs.* temperature ($O_2 : C_2H_6 = 0.14$; $H_2O : C_2H_6 = 1.0$; GHSV = 7370 h^{-1}) (*a*, *b*) and *vs.* $O_2 : C_2H_6$ ratio ($T = 800$ °C; $H_2O : C_2H_6 = 1.0$; GHSV = 7370 h^{-1}) (*c*, *d*).[64]
Reactants: ethane (*1*), O_2 (*2*); products: ethylene (*3*), CO (*4*), methane (*5*), propylene (*6*), C_{3+} alkanes (*7*), butylene (*8*), CO_2 (*9*).

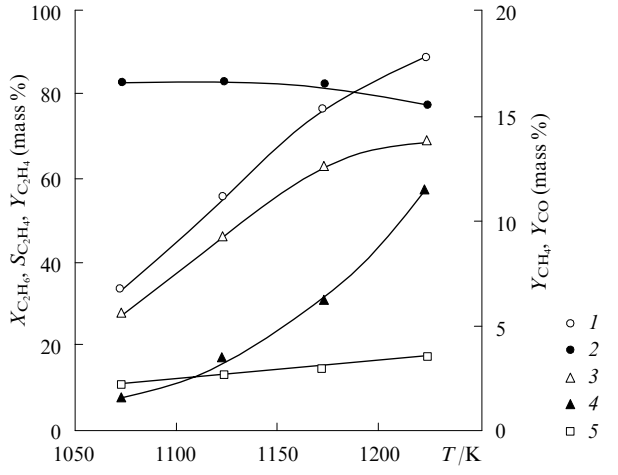


Figure 29. Ethane conversion (*X*) and product selectivities (*S*) and yields (*Y*) *vs.* temperature in the corundum reactor ($p = 1.4$ atm, $[O_2] = 5\%$, $t = 0.2$ s, steam : ethane = 0.3).[65]
(*1*) $X_{C_2H_6}$, (*2*) $S_{C_2H_4}$, (*3*) $Y_{C_2H_4}$, (*4*) Y_{CH_4}, (*5*) Y_{CO}.

in the ethylene yield at an oxygen concentration of $> 5\%$ (Fig. 30). Almost all oxygen reacts to be converted to CO, which accounts for the proportional increase in the CO yield and the decrease in the selectivity of ethylene formation following an increase in the oxygen content. Meanwhile, the oxygen content barely affects the yields of acetylene, propane and propylene; only traces of CO_2 were detected (not more than 0.3 mass %).

When the oxygen concentration was raised from 0% to 15%, heat evolved upon oxidation allowed the reactor heating temperature to be decreased by approximately 60 degrees. But the addition of oxygen had almost no influence on the yields of products except for carbon monoxide and water. Analysis of by-products showed that the yield of acetylene usually did not exceed 1 mass % and only at the highest experimental temperature (1273 K), it reached 3 mass %. The yield of propylene was ~ 1 mass % and almost did not depend on the reaction time, the temperature or oxygen concentration. The yield of propane was < 0.5 mass % in all experiments. The highest yield of butenes was 2 mass%. The yield of C_5 products ranged

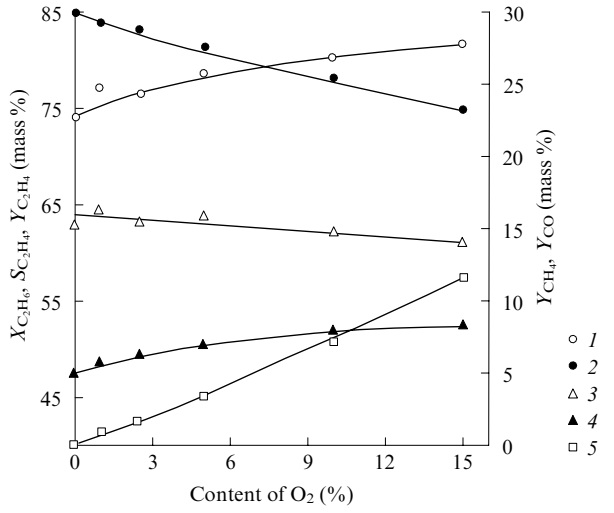


Figure 30. Ethane conversion (X) and product selectivities (S) and yields (Y) in the corundum reactor *vs.* oxygen content (p = 1.4 atm, T = 1173 K, t = 0.2 s, steam : ethane = 0.3).[65]
(*1*) $X_{C_2H_6}$, (*2*) $S_{C_2H_4}$, (*3*) $Y_{C_2H_4}$, (*4*) Y_{CH_4}, (*5*) Y_{CO}.

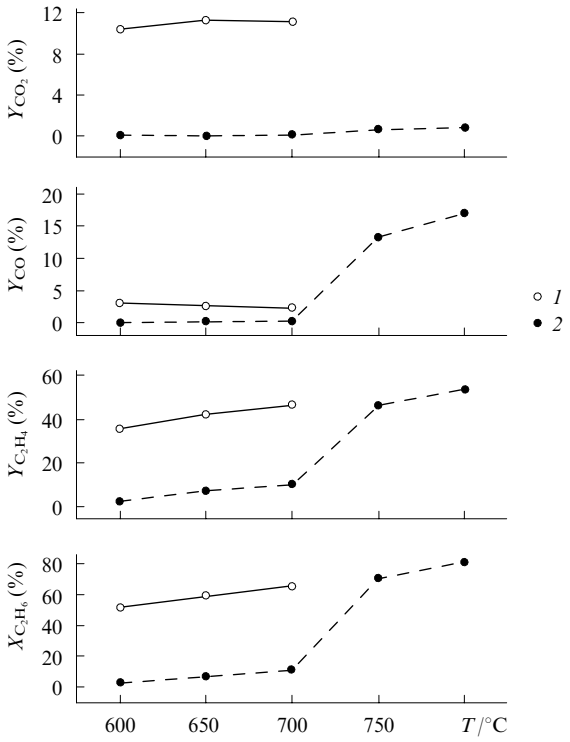


Figure 31. Effect of temperature on ethane conversion and yields of C_2H_4, CO and CO_2 in the presence (*1*) and in the absence (*2*) of the $SrLaNdO_x$ catalyst ($C_2H_6 : O_2 : H_2O$ = 2 : 1 : 1.5, reactant flow rate 60 ml min^{-1}).[66]

from 0.1 mass % to 0.5 mass%, and that of C_{6+} was 0.1 mass % to 2 mass%. Generally, their yield increased with temperature but did not depend on the oxygen content. No oxygenate formation was observed. The ethane conversion and the ethylene yield in the stainless-steel reactor (Incoloy 800) were ~5% lower than the values obtained in the corundum reactor under the same conditions.

Although it was specially noted that the conversion of oxygen was complete in all experiments, the experimental results and the process modelling prompt the conclusion that the oxidation does not end in the narrow zone near the reactor inlet but occurs through a considerable part of the reactor. It was decided that by adding oxygen it would be possible to increase ethane conversion by 10% – 20% per pass (up to 68.8% – 80.9 mass % *vs.* usual 60% – 65%) and to increase the yield of ethylene by more than 5% (from 55.2 mass % to 60.4 mass %) in industrial pyrolysis units. However, this increase in the ethylene yield is attained at the expense of decreasing selectivity of its formation from 80.2 mass % to 74.7 mass %.[65]

A comparative study of the catalytic and non-catalytic oxidative dehydrogenation of ethane to ethylene at temperatures of 600 – 800 °C and a $C_2H_6 : O_2$ ratio from 2 to 8 was reported. [66] As the catalyst, $SrLaNdO_x$ was used. Although 600 °C is usually considered to be the boundary between the gas-phase and the catalytic process, in this study carried out with moderate free space in the reactor, up to 700 °C, the contribution of the gas-phase process was insignificant as compared with the catalytic process, which provided the highest yield of ethylene (46%) at 71% selectivity at this temperature. Above 700°C, the gas-phase process became predominant and provided the ethylene yield of 46% (selectivity 66%) at 750 °C or 53% (selectivity 65%) at 800 °C. At these temperatures, the ethane conversion could be as high as 60% – 80% despite the short reaction time (0.2 s). Thus, the presence of the catalyst decreased the temperature at which the highest yield was achieved by approximately 50 degrees but this yield was lower (Fig. 31).

The primary difference between the product distributions in the heterogeneous and homogeneous reactions was the minor formation of carbon dioxide in the homogeneous reaction. This is noted in the vast majority of studies and convincingly indicates that under these conditions, CO_2 is mainly formed in heterogeneous processes. One more important difference is that in the catalytic process, the selectivity of ethylene formation increases following the increase in the ethane conversion, whereas in the gas-phase process, the selectivity is maximized at low conversion (Fig. 32). Thus, in the gas-phase process, as opposed to the catalytic process, ethylene is the primary conversion product. In addition, complete conversion of oxygen in the catalytic reaction is already attained at 600 °C, whereas in the gas-phase process, it is only 80% even at 750 °C. The mechanism of oxygen conversion and the role of the surface in this event are still obscure.

The addition of 30% of steam to the reaction mixture affected only slightly both the catalytic and the gas-phase processes (see Fig. 32). In the presence of steam, the ethane conversion slightly increased (by 5% – 10%), first of all, for the formation of more CO. The selectivity towards ethylene remained almost invariable. Thus, the addition of steam only increases the contribution of steam reforming, which nevertheless remains low as compared with the oxidative dehydrogenation.

The homogeneous and heterogeneous (catalyzed by 20 mass % MoO_3/Al_2O_3) oxidative and thermal dehydrogenation of ethane were studied using the temperature-programmed reaction.[67] The experiments were carried out at steady flow conditions with a 15 °C min^{-1} linear increase

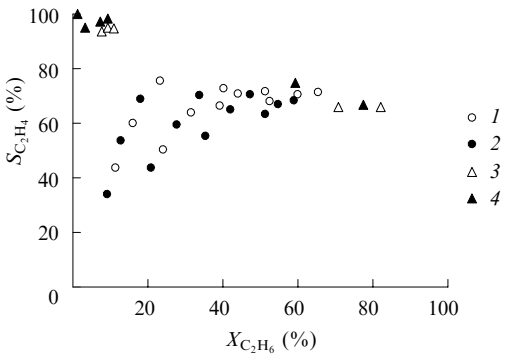


Figure 32. Selectivity of ethylene formation *vs.* ethane conversion in catalytic (*1*, *2*) and non-catalytic (*3*, *4*) processes.[66]
(*1*, *3*) No steam addition; (*2*, *4*) addition of 30% of steam.

in temperature up to 700 °C. The reaction products were analyzed by mass spectrometry. The authors proceeded from the fact that the reaction on Al_2O_3-supported molybdenum catalysts follows the Mars and van Krevelen type redox mechanism, which implies reduction of the catalyst by alkane with extraction of the lattice oxygen followed by re-oxidation of the reduced catalyst by molecular oxygen. Due to the low reactivity of alkanes, the C–H bond activation occurs only at high temperature and is the rate-determining step of the whole process. At subsequent steps, homogeneous reactions, which are highly selective towards alkenes, play a significant role but the total yield of alkenes may depend to a large extent on their subsequent oxidation. Therefore, one of the goals of that study was to elucidate the contribution of this reaction. To eliminate secondary reactions, experiments were carried out with highly dilute mixtures (2% of the hydrocarbon and 2% of oxygen in helium). The residence time of the reactants in the empty reactor under standard conditions (20 °C, 1 atm) was ~6 s.

As in most other works, the gas-phase oxidative dehydrogenation of ethane occurred only starting from 650 °C to give nearly equal quantities of C_2H_4 and H_2. In addition, at 655 °C, CO and H_2O were detected, together with smaller amounts of CH_4 and CO_2. The signal of O_2 simultaneously decreased, indicating participation of oxygen in the gas-phase reaction. The gas-phase oxydehydrogenation was highly selective towards ethylene; the selectivity of ethylene formation was more than 95% at low ethane conversion and remained >60% at ethane conversions of up to 80% (at 700 °C). The main by-product was CO, which was evidently formed in secondary alkene oxidation reactions, as the selectivity of its formation increased with conversion. The low selectivity of CO_2 formation (<2%) virtually did not change with increasing temperature and conversion. In the authors' opinion, this implies that this product is formed upon deep oxidation of ethane in an early step. However, in our opinion, continuous formation of CO_2 in heterogeneous processes on the reactor surface is more likely.

The radical mechanism of the gas-phase oxidative dehydrogenation of ethane has been discussed in many publications. The formation of key products may be interpreted by the following reactions:[67]

$$C_2H_6 \longrightarrow 2CH_3^{\bullet}$$

$$C_2H_6 + O_2 \longrightarrow C_2H_5^{\bullet} + HO_2^{\bullet}$$

$$C_2H_5^{\bullet} \longrightarrow C_2H_4 + H^{\bullet}$$

$$C_2H_5^{\bullet} + O_2 \longrightarrow C_2H_4 + HO_2^{\bullet}$$

$$C_2H_6 + HO_2^{\bullet} \longrightarrow C_2H_5^{\bullet} + H_2O_2$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$$

$$H_2O_2 \longrightarrow 2OH^{\bullet}$$

$$C_2H_6 + H^{\bullet} \longrightarrow C_2H_5^{\bullet} + H_2$$

$$C_2H_6 + OH^{\bullet} \longrightarrow C_2H_5^{\bullet} + H_2O$$

$$C_2H_6 + CH_3^{\bullet} \longrightarrow C_2H_5^{\bullet} + CH_4$$

In addition, radical recombination reactions and subsequent oxidation of the resulting ethylene and hydrogen, mainly to CO and H_2O, take place.

A comparison of the gas-phase process with experiments in the presence of the MoO_3/Al_2O_3 catalyst demonstrated[67] that the catalytic process starts at a lower temperature (by ~160 degrees). As in the gas-phase process, ethane oxydehydrogenation gave ethylene as the primary product; however, under these conditions at temperatures of up to 600 °C ethylene is completely oxidized to CO. The delay of appearance of CO_2 with respect to CO indicates that CO_2 is the product of CO oxidation. The fact that no oxidation of CO to CO_2 occurs in the gas-phase processes means that this is entirely due to the catalyzed process. At 700 °C, ethane conversion reached 75% and was apparently limited by complete conversion of oxygen. The selectivities of formation of C_2H_4, CO and CO_2 were 52%, 26% and 22%, respectively. The authors assume that the activation of ethane on the catalyst is accompanied by the formation of surface ethoxide the transformations of which produce the major reaction products in the temperature range of up to 650 °C:

$$C_2H_6 \longrightarrow [C_2H_5O]_{(s)} + [OH]_{(s)}$$

$$[C_2H_5O]_{(s)} \rightleftharpoons [C_2H_4]_{(s)} + [OH]_{(s)} \rightleftharpoons C_2H_4$$

$$\Big\downarrow\Big\uparrow$$

$$[CH_3COO]_{(s)} + [HCOO]_{(s)} \longrightarrow CO_x$$

According to this scheme, increase in the amount of ethylene in the gas phase following the increase in the ethane conversion shifts the reaction equilibrium to the left and results in oxidation of some of ethylene to surface formates and acetates, which, in turn, precede the formation of CO_x. Thus, the ethyl radicals formed on the catalyst can either desorb to the gas phase, which is facilitated by higher temperature, and undergo radical chain transformations, or react on the surface to give ethoxides, which either decompose to give ethylene or are further oxidized to CO_x.

Heracleous and Lemonidou[67] also investigated the homogeneous and heterogeneous oxidation of the major dehydrogenation product, ethylene. A measurable conversion of ethylene was observed in the homogeneous reaction only above 670 °C, *i.e.*, at higher temperatures than found for ethane. This is consistent with known data about high stability of ethylene, which distinguishes it from heavier alkenes, which are usually more reactive than the corresponding alkanes. The conversion of ethylene above 670 °C is accompanied by the formation of mainly CO and H_2O and lesser amounts of H_2, CH_4 and CO_2. Thus, the principal reaction that takes place is ethylene oxidation to CO with a selectivity of nearly 90%. Since at 700 °C, the rate of ethane

consumption was twice greater than the rate of ethylene consumption, the higher thermal stability of ethylene was thus responsible for its higher yield in the gas-phase process. Conversely, in the catalytic reaction, ethylene readily reacted with O_2 even at 290 °C, that is, at a temperature 200 degrees lower than the temperature needed to activate ethane. Thus, the decrease in the selectivity of ethylene formation upon the catalytic oxydehydrogenation of ethane is caused most of all by its subsequent heterogeneous oxidation. The authors discuss the reaction mechanism and the possible role of the lattice and gas-phase oxygen in the reaction. In the authors' opinion, lattice oxygen selectively activates ethane but feebly reacts with ethylene. Meanwhile, the presence of gas-phase oxygen on the catalyst surface leads to formation of more labile forms of adsorbed oxygen responsible for fast decomposition of ethylene. Therefore, ethylene decomposes faster than ethane and the selectivity of ethylene formation is low.

An important observation made in the cited study is that in both the absence and the presence of oxygen, the primary pathway to ethylene in the homogeneous reaction is the pyrolysis of ethane to give ethylene and hydrogen. The authors performed a comparative study of the thermal pyrolysis of ethane under the same conditions. In the oxygen-free pyrolysis, which started at 610 °C, intensive soot formation was noted and, hence, a higher hydrogen yield relative to the ethylene yield. The moderate yields of methane (selectivity $< 1\%$) and higher hydrocarbons (selectivity $< 0.9\%$), which were observed at 670 °C, can be attributed to some contribution of the thermal cracking of ethane. The rates of all reactions increase with temperature, and at 700 °C, the conversion of ethane reaches 44%. No secondary reactions were detected, which confirms the high stability of ethylene in the gas phase. It was shown in special experiments that in the absence of oxygen, no noticeable pyrolysis of ethylene is observed up to 700 °C, which is in line with higher activation energy of its thermal decomposition compared to the activation energy of thermal decomposition of ethane and accounts for the high yield of ethylene upon thermal pyrolysis.

Curiously, dehydrogenation of ethane starts at a 40 degrees lower temperature in the absence of oxygen than in the presence of oxygen (Fig. 33). Actually, one can speak about a slight inhibiting effect of oxygen at an early stage of the reaction. However, later, oxygen substantially increases the conversion, which can reach 75% in the presence of oxygen at 700 °C, while without oxygen it is only 44%.

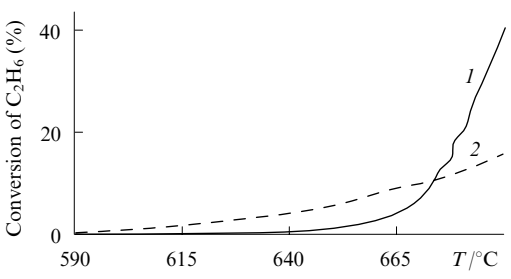


Figure 33. Comparison of thermal conversion of ethane in the presence (*1*) and in the absence (*2*) of oxygen.[67]

The intricate influence of oxygen on dehydrogenation is caused, on the one hand, by acceleration of radical generation as a result of oxygen reaction with ethane, and on the other hand, by the reaction of oxygen with ethyl radicals to give ethylene and inactive $HO_2^{\bullet}$ radical, which mainly induces chain termination on reactor walls. However, when the radical generation is intensive, the homogeneous recombination of $HO_2^{\bullet}$ radicals followed by the formation of reactive $OH^{\bullet}$ radicals and the corresponding acceleration of the reaction become important. A similar effect was observed for the oxidative pyrolysis of propane.[26]

The gas-phase oxidative conversion of propane to alkenes under atmospheric pressure was compared[68] with the conversion catalyzed by lithium-promoted magnesium oxide (Li – MgO). An increase in the propane concentration in an empty reactor resulted in exponential increase in the yields of all products (Fig. 34). Thus, the apparent order of the reaction increased with increase in the propane pressure. For the partial pressure of propane of < 0.2 bar, no CO or H_2 formation was observed.

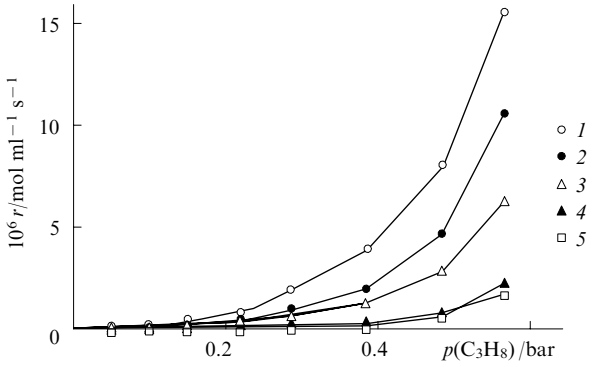


Figure 34. Formation rates (r) of products of the oxidative conversion of propane in an empty reactor *vs.* propane partial pressure.[68]
$p(CO_2) = 0.02$ bar; $p(O_2) = 0.14$ bar; $T = 600$ °C; reactant flow rate 100 ml min^{-1}, cylindrical reactor volume 0.25 ml.
(*1*) Propylene, (*2*) ethylene, (*3*) methane, (*4*) CO, (*5*) H_2.

The dependences of the product formation rates on the partial pressure of oxygen in the empty reactor (Fig. 35) and in the catalyst-loaded reactor were the same. In both cases, the rate of pyrolysis rapidly increased at low oxygen concentrations; however, without the catalyst, the rate of CO formation was four times lower.

Whereas in the presence of the catalyst, the conversion of propane follows a linear dependence on the reaction rate, in the empty reactor, the conversion grows exponentially at short times, and the whole dependence is S-shaped due to oxygen consumption (Fig. 36). Thus, under certain conditions, conversion in the empty reactor is greater than that in the catalyst-loaded reactor. Carbon dioxide, which strongly inhibits the catalytic reaction, had no influence on the gas-phase reaction.

Ethane oxypyrolysis was investigated[69] also under adiabatic compression (maximum compression ratio of 16 to 57) over $\sim 1-5$ ms at an initial temperature of 120 °C and an initial pressure of 1 atm in a highly dilute mixture (2% C_2H_6, 0.35 – 1.05% O_2, and the rest is N_2). On pulse heating to ~ 1090 °C, the ethane conversion within a milli-

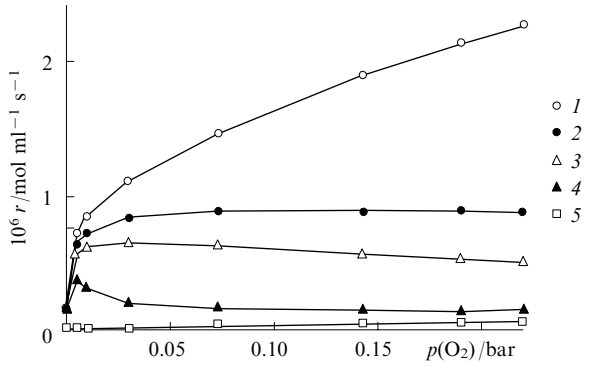


Figure 35. Formation rates (r) of products of the oxidative conversion of propane in an empty reactor *vs*. oxygen partial pressure.[68]
$p(CO_2)$ = 0.02 bar; $p(C_3H_8)$ = 0.28 bar; T = 600 °C; reactant flow rate 100 ml min^{-1}, cylindrical reactor volume 0.25 ml.
(*1*) Propylene, (*2*) ethylene, (*3*) methane, (*4*) H_2, (*5*) CO.

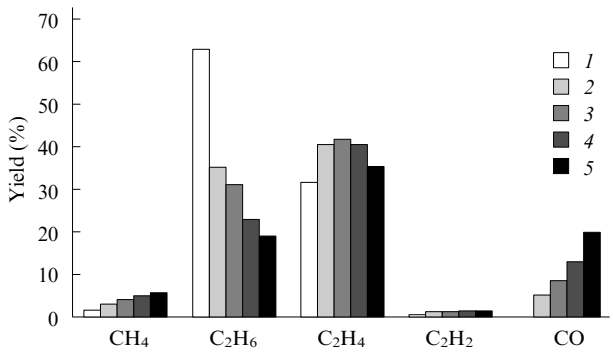


Figure 37. Effect of oxygen admixtures on the yields of ethane oxypyrolysis products in an adiabatic compression reactor.[69]
Mixture: 2% C_2H_6, 0–1.05% O_2, the rest N_2. T_{init} = 120°C, p_{init} = 1 atm, T_{max} = 1050 °C, p_{max} = 120 atm. Initial oxygen concentration ($O_2 : C_2H_6$ ratio): 0 (0) (*1*); 0.35 (0.175) (*2*); 0.53 (0.263) (*3*); 0.70 (0.35) (*4*); 1.05 (0.525) (*5*).

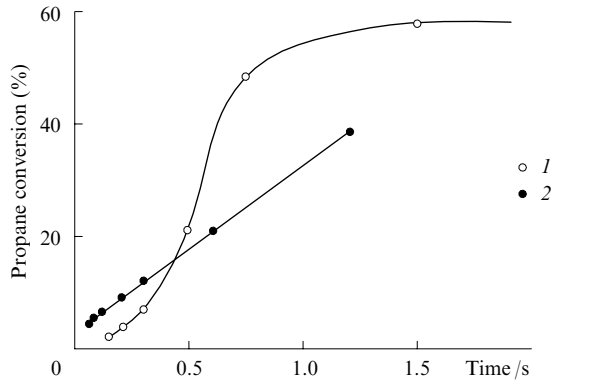


Figure 36. Propane conversion *vs*. reaction time in an empty reactor (*1*) and in the presence of a catalyst (*2*).[68]
$p(C_3H_8)$ = 0.28 bar; $p(O_2)$ = 0.14 bar; T = 600 °C; reactant flow rate 100 ml min^{-1}, cylindrical reactor volume 0.25 ml.

second period (62%) was comparable with that in industrial reactors over long periods of time. The selectivity of ethylene formation was 75%. Ethylene and hydrogen were the major products, and carbon monoxide and methane were the most significant by-products. Comparison of the data obtained under comparable conditions shows that oxygen admixtures, apart from increasing the ethane conversion (decreasing the temperature at which the same conversion is attained by 60–90 degrees), also decrease the selectivity of ethylene formation and increase the selectivity towards CO and CH_4 (Fig. 37). The yield of ethylene passes through a maximum. Carbon dioxide and soot were virtually absent in the products of oxypyrolysis.

Thus, comparison of heterogeneous and homogeneous oxypyrolysis of C_2–C_4 alkanes demonstrates that raising the temperature induces a fairly sharp transition of the heterogeneous mechanism to the homogeneous mechanism, which is accompanied by the corresponding change in the product composition, first of all, a decrease in the selectivity towards CO_2 and an increase in the selectivity towards ethylene.

IV. Oxidative pyrolysis of C_5–C_6 alkanes

Nowadays the oxycracking of C_{5+} alkanes attracts considerable attention as a potential source of valuable chemical products, first of all, alkenes, alternative to the complex and power intensive pyrolysis of alkanes.[70–73] Most of all, the catalytic oxidative cracking (COC) is considered. The advantages of the COC over pyrolysis are associated with the following factors: (i) decrease in the heat removal rate and the possibility of conducting the process in the autothermal mode; (ii) shift of the equilibrium between alkanes and alkenes towards higher yields of alkenes; (iii) acceleration of the radical chain reactions in the gas phase; (iv) reduced soot formation. However, the design of effective catalysts for this process is a fairly complicated task. In addition to catalysis of the key process, it is necessary to prevent further oxidation of the formed alkenes, which are more reactive than the starting alkanes. The vast majority of publications on this subject are devoted to the oxidative cracking of hexane, which is considered as a convenient model of petrol type alkanes.

A promising catalyst for the oxidative cracking of hexane is Li–MgO prepared by the sol–gel method and promoted by MoO_3.[72,73] Depending on the process conditions, a broad spectrum of products is formed, the selectivity of formation of light alkenes being high (Fig. 38).

Oxygen, even when present in a low concentration, substantially increases the conversion of hexane and the selectivity of CO formation, mainly at the expense of C_1–C_4 alkanes. The selectivity of formation of C_2–C_4 alkenes varies insignificantly (Figs 39, 40).

The pronounced effect of oxygen present in concentrations of up to 4% on the conversion of hexane (see Fig. 39) is attributed to its role in regeneration of the catalyst active sites by removing the hydrogen present as [Li^+OH^-] from the surface.

$$2\,Li^+OH^- + \frac{1}{2}O_2 \longrightarrow 2\,Li^+O^- + H_2O$$

The subsequent moderate increase in the hexane conversion upon increase in the oxygen concentration is attributed to its role in the acceleration of gas-phase radical

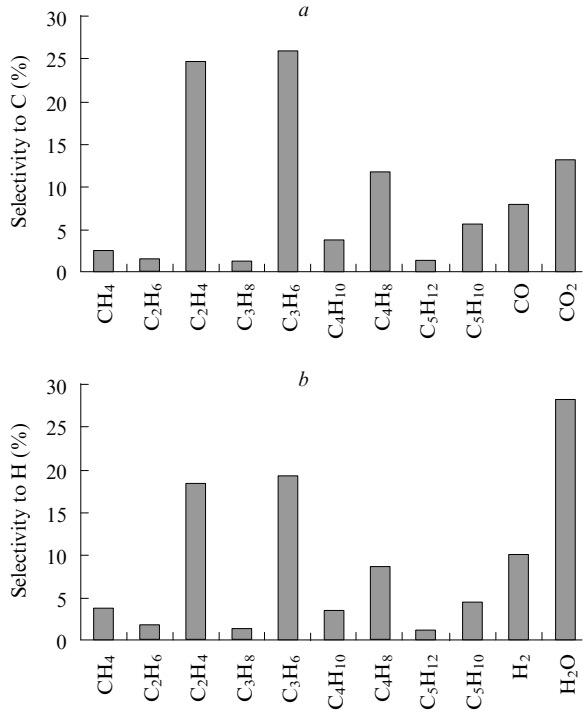


Figure 38. Distribution of products of hexane catalytic oxidative cracking.[73]
(*a*) Selectivity to C, (*b*) selectivity to H.
Conditions: reactant flow rate 100 ml min^{-1}; [C_6H_{14}], 10%; [O_2], 8%; the rest is helium; T = 575 °C, Li–MgO catalyst (300 mg), hexane conversion, 45%.

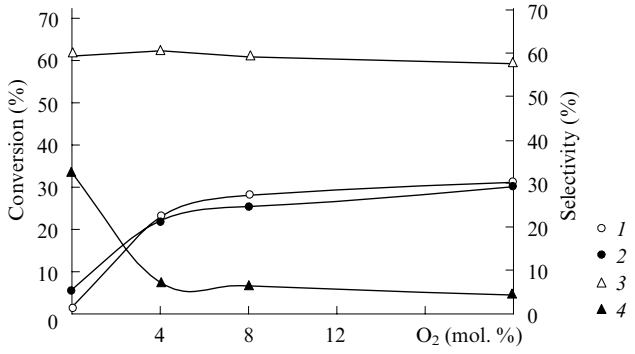


Figure 39. Effect of the oxygen concentration on hexane conversion and product selectivities in the catalytic oxycracking of hexane.[72]
(*1*) Hexane conversion, (*2*, *3*, *4*) selectivities to CO_x, light C_2-C_4 alkenes and C_1-C_4 alkanes, respectively. Conversion of O_2 = 68.5 mol.%, 65.2 mol.% and 38.5 mol.% for O_2 concentrations of 4 mol.%, 8 mol.% and 20 mol.%, respectively. Hexane concentration: 10% in He, T = 575 °C; Li–MgO catalyst.

processes due to the formation of $HO_2^{\bullet}$ radicals and the subsequent reactions involving them.

$$C_nH_{2n+1}^{\bullet} + O_2 \longrightarrow C_nH_{2n} + HO_2^{\bullet}$$

However, a nearly the same selectivity towards C_2-C_4 alkenes as in the catalytic oxidative cracking can also be

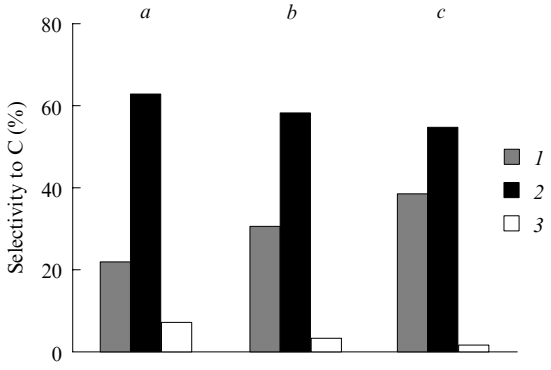


Figure 40. Effect of the oxygen concentration on the selectivity towards CO_x (*1*), light C_2-C_4 alkenes (*2*) and C_1-C_4 alkanes (*3*) in the catalytic oxycracking of hexane.[72]
Concentration of O_2 = 4 mol.% (*a*), 8 mol.% (*b*) and 20 mol.% (*c*); O_2 conversion is 68.5 mol.%, 40.5 mol.% and 23.5 mol.%, respectively. Initial hexane concentration, 10% in He; hexane conversion, 17%; T = 575 °C; Li–MgO catalyst.

attained in the gas-phase oxidative cracking under atmospheric pressure (GOC) (Fig. 41).

Figure 42 shows a comparison of the temperature dependences of gas-phase oxidative cracking and pyrolysis of hexane, and Figure 43 compares analogous temperature dependences of the gas-phase oxycracking of hexane and the catalytic oxycracking of hexane in the presence of typical catalysts for oxidative condensation of methane (OCM) and carbon dioxide reforming of methane (CDRM).

Comparison of these data shows that the oxycracking of hexane in the gas phase becomes noticeable above > 500 °C, and above 700 °C it predominates. Despite the substantial differences between the hexane and oxygen concentrations in the gas-phase oxycracking of hexane aimed at the preparation of alkenes[70–72] (where $C_6H_{14}:O_2$ = 0.7–0.8) and in the oxygen-activated gas-phase pyrolysis of hexane aimed at selective conversion of the minor hexane admix-

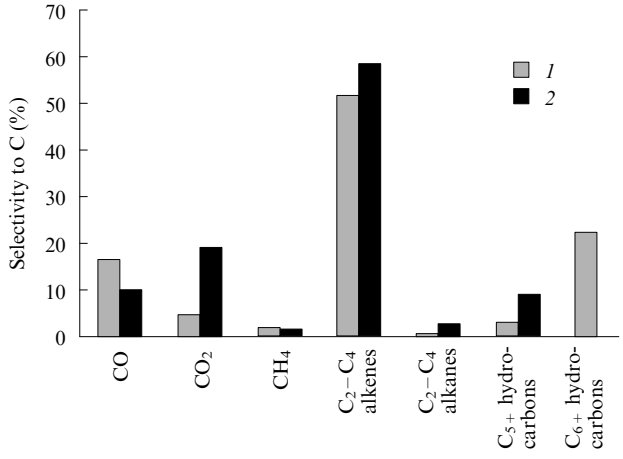


Figure 41. Selectivity of product formation in the gas-phase oxidative cracking (*1*) and catalytic oxidative cracking (*2*) on the Li–MgO catalyst.[72]
Hexane conversion, 30%; mixture composition: hexane, 10%; oxygen, 20%; the rest is helium; T = 575 °C.

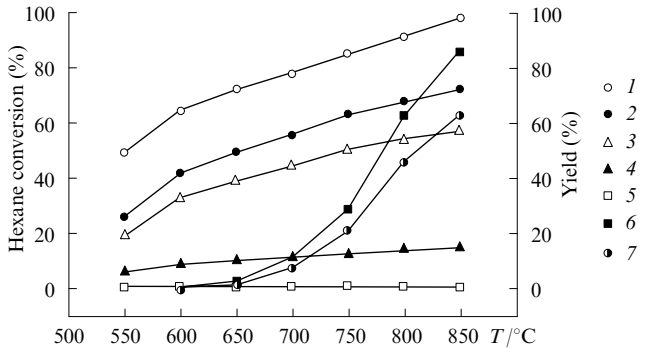


Figure 42. Hexane conversion and product yields *vs.* process temperature for GOC and hexane pyrolysis ($C_6H_{14}:O_2 = 0.8$ without dilution with inert gas for GOC and with dilution with 55.6% of N_2 for pyrolysis).[70]
GOC: (*1*) hexane conversion, (*2*, *3*, *4*, *5*) yields of alkenes and CO, alkenes, CO and CO_2, respectively. Pyrolysis: (*6*) hexane conversion, (*7*) alkene yield.

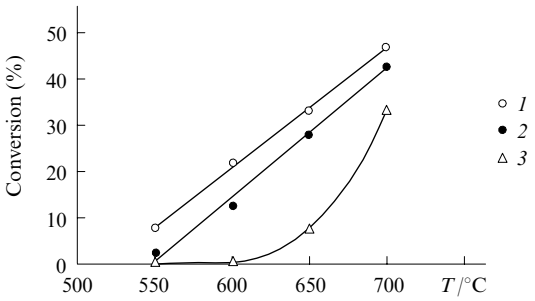


Figure 43. Hexane conversion in nitrogen *vs.* temperature in the presence of OCM catalysts (*1*) ($N_2:O_2 = 96.0:4.0$) and CDRM catalysts (*2*) ($N_2:O_2 = 96.7:3.3$) and in empty reactor (*3*) ($N_2:O_2 = 96.6:3.4$).[74]
Reactor diameter 3 mm, mixture flow rate 7 ml min^{-1}.

ture ($C_6H_{14}:O_2 = 3.75$),[74] the key features of these processes are correlated with each other. The presence of oxygen has a considerable effect on the reaction kinetics by increasing the conversion of hexane (Fig. 44) or by decreasing the process temperature.

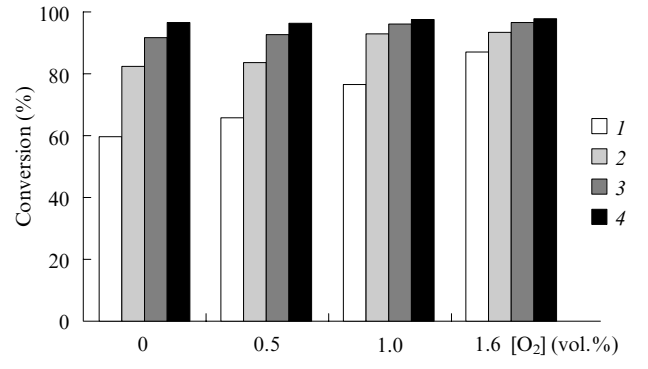


Figure 44. Hexane conversion in methane in the empty reactor 6 mm in diameter at 730 °C *vs.* oxygen content at different reactant residence times.[74]
Reaction time: 0.75 (*1*), 1.66 (*2*), 3.31 (*3*), 7.10 s (*4*).

When $C_6H_{14}:O_2 = 0.8$, a nearly the same conversion of hexane is achieved at a temperature 200 degrees lower than in the oxygen-free pyrolysis (see Fig. 42).[70] In the studies[70,74] carried out in the presence of oxygen at a reaction time of ~1 s, a hexane conversion of ~90% was attained at a temperature of ~750 °C where the gas-phase pyrolysis of hexane is insignificant. Since dilution of a hexane – oxygen mixture with nitrogen, all other factors being the same, slightly increases the conversion,[70] the oxidation of a minor hexane admixture in nitrogen and methane should proceed under highly favourable conditions. This may be responsible for the fact that Arutyunov *et al.*[74] achieved the same conversion at a much lower content of oxygen relative to hexane (at higher $C_6H_{14}:O_2$ ratio).

According to Arutyunov *et al.*[74] the effect of oxygen on the conversion of hexane rapidly drops as the oxygen concentration increases (see Fig. 44); however, the results of Liu *et al.*[70] do not confirm this trend (Fig. 45).

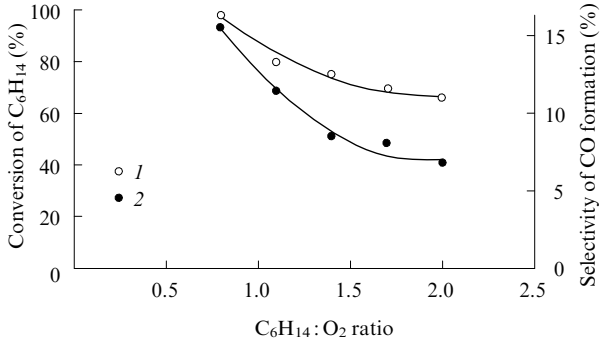


Figure 45. Hexane conversion (*1*) and selectivity of CO formation (*2*) *vs.* $C_6H_{14}:O_2$ ratio in the oxidative cracking of C_6H_{14}.[70]

In both works, the major products of hexane conversion in the presence of oxygen were lighter alkenes and alkanes and carbon oxide, the overall selectivity towards which was 60% – 70%. The selectivity of formation of alkenes depends little on the concentration of oxygen,[72] but the selectivity of CO formation rapidly decreases with increase in the $C_6H_{14}:O_2$ ratio.[74] According to Boyadjian *et al.*,[72] in the catalytic reaction, this is accompanied by the corresponding increase in the selectivity of alkane formation (see Fig. 40). Arutyunov *et al.*[74] almost did not observe the formation of carbon dioxide in the gas-phase reaction, while in the work by Liu *et al.*,[70] its concentration was 16 times lower than the concentration of CO. In the presence of a catalyst, as in the catalytic oxydehydrogenation, carbon dioxide became the predominant carbon oxide both according to the data of Arutyunov *et al.*[74] and in the direct catalytic oxycracking aimed at the preparation of alkenes,[72] probably due to heterogeneous deep oxidation on the catalyst surface.

An increase in the oxygen concentration in the gas-phase reaction leads to an increase in both the hexane conversion and the selectivity of CO formation (see Fig. 45), although these dependences are evidently non-linear. Note that at sufficiently high temperature, gas-phase conversion is no less efficient than catalytic conversion (see Fig. 43). An important practical consequence of the presence of oxygen

in the mixture is the absence of soot formation in the oxidative pyrolysis.

The characteristic times of hexane oxidative cracking under atmospheric pressure and a temperature of >700 °C are about a second (Fig. 46).

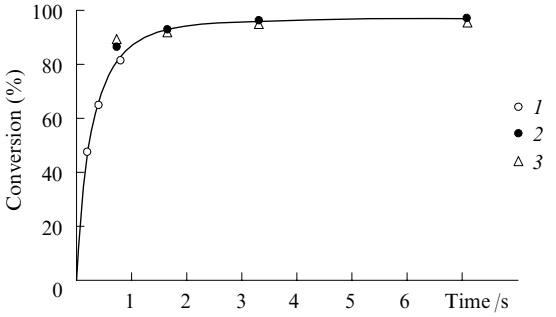


Figure 46. Hexane conversion at 730 °C *vs.* reactant residence time in an empty reactor.[74]
Mixture with nitrogen at $[O_2] = 3.4\%$ and reactor diameter of 3 mm (*1*) and 6 mm, (*2*); mixture with methane at $[O_2] = 1.6\%$ and reactor diameter of 6 mm (*3*).

It is useful to compare the data on hexane oxypyrolysis with the experimental results and kinetic modelling data on oxygen-free gas-phase pyrolysis of hexane under atmospheric pressure (reaction time of ~ 5 s, $T = 550-675$ °C).[75] Although the conversion and the composition of products (except for oxygenates) are similar to those for oxypyrolysis (Table 5), this process is accompanied by heavy soot formation. It should be emphasized that the change in the molar content of hexane and other products (see Table 5) is due not only to the reactions that take place but also to the increase in the total number of gas moles in the system during the reaction. This is especially pronounced at high temperatures, as can be clearly seen from nitrogen data.

The key products include H_2, methane, ethylene, ethane, propylene and C_4 and C_5 hydrocarbons. The sum of methane, ethylene and propylene accounts for more than 70% of the total yield of products at any studied temperature. Among C_3 hydrocarbons, more than 90% are represented by propylene. The mole fractions of C_4 and C_5 hydrocarbons, unlike other products, already start to decrease at ~ 650 °C. This may be caused by either their cracking to give lighter hydrocarbons or condensation to give soot precursors; intensive soot formation is indicated by the fact that the reactor walls are coated by black deposits at high temperature spots. The temperature dependences of hexane and product concentrations predicted by the kinetic model are shown in Fig. 47.

Table 5. Experimental product distribution for pyrolysis of n-hexane [as a mixture with nitrogen (mol.%)] ($t \approx 5$ s, $p \approx 1$ atm).[75]

Products	Temperature /°C				
	550	600	625	650	675
H_2	0.2	1.2	2.2	3.4	4.9
CH_4	1.6	6.0	10.3	15.4	20.0
C_2H_4	1.2	6.0	11.7	16.9	23.6
C_2H_6	0.8	2.7	4.2	5.3	5.9
ΣC_3	1.3	5.1	8.9	11.3	12.0
ΣC_4	0.7	2.4	3.3	3.4	2.5
ΣC_5	0.1	0.5	0.7	0.6	0.3
ΣC_6	47.9	33.7	22.7	12.2	5.3
N_2	46.7	40.5	34.5	26.2	22.2
Total	100.4	98.2	98.5	94.6	96.8

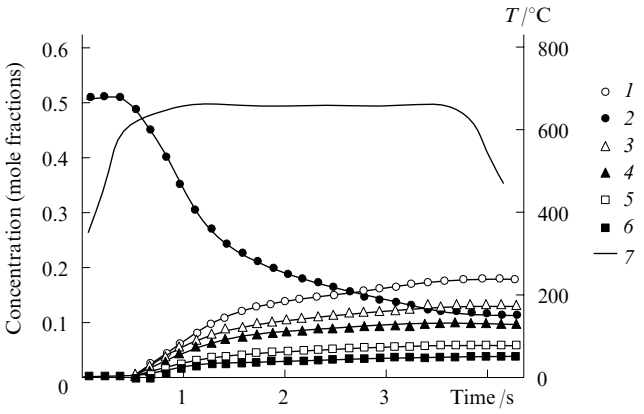


Figure 47. Calculated dependences of the concentrations of n-hexane and pyrolysis products *vs.* residence time in the reactor at 650 °C.[75]
(*1*) n-Hexane, (*2*) ethylene, (*3*) methane, (*4*) propane, (*5*) ethane, (*6*) H_2. Temperature profile along the reactor length is shown (*7*).

Liu *et al.*[76] noted that the gas-phase oxidative cracking of hexane at 750 °C resulted in much higher conversions (85%) and alkene yields (51%) than pyrolysis (29% and 21%, respectively). The same publication describes a comparative study of the gas-phase oxidative cracking and pyrolysis of cyclohexane in a quartz reactor with a 6 mm inner diameter and a 30 cm length under atmospheric pressure, at a 0.5–1.4 s reaction time and cyclo-$C_6H_{12}:O_2 = 0.8$. In the absence of oxygen below 750 °C, decomposition of cyclohexane is not observable. Even at 800 °C, conversion reaches only 38.8%. This gives two major alkenes, ethylene and butadiene, the concentration of the latter remaining much lower than the concentration of the former until the temperature exceeds 850 °C. At the same temperature, the highest yield of alkenes (54%) is achieved. The results (Fig. 48) show that up to 850 °C, the selectivity of alkene formation is higher in oxycracking than in pyrolysis, while the selectivity towards butadiene is lower in oxycracking than in pyrolysis. This indicates that in the presence of oxygen, cracking becomes more extensive, being accompanied by cleavage of a greater number of C–C bonds to give lighter molecules. However, despite the high conversion of cyclohexane in the oxycracking and high yield of alkenes, the overall selectivity towards unsaturated hydrocarbons is lower than in the pyrolysis due to the formation of CO_x. The selectivity towards CO_2 is $<1\%$, whereas the selectivity towards CO may reach 16%.

In this process, too, the ratio cyclo-$C_6H_{12}:O_2$ is the key parameter. In experiments, it was varied from 0.5 to 2.0 (Fig. 49), *i.e.*, it was much higher than the stoichiometric ratio for complete oxidation equal to 0.11.[76]

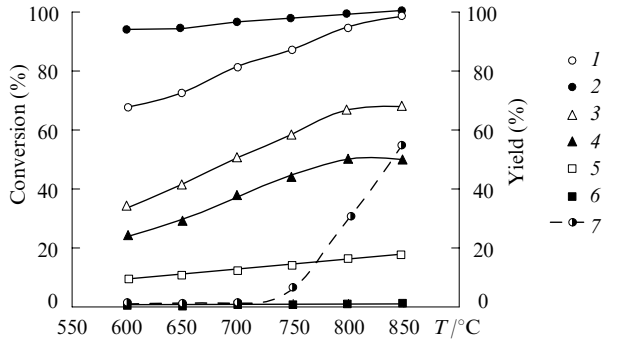


Figure 48. Temperature dependences of cyclohexane conversion and product yields in the oxycracking at cyclohexane : O_2 = 0.8 and reactant flow rate of 120 ml min^{-1}.[76]
Conversion: C_6H_{12} (*1*) and O_2 (*2*); yields: CO + alkenes (*3*), alkenes (*4*), CO (*5*), CO_2 (*6*). For comparison, the yield of alkenes upon cyclohexane pyrolysis is shown (cyclohexane + 55.6% of N_2, reactant flow rate 120 ml min^{-1}) (*7*).

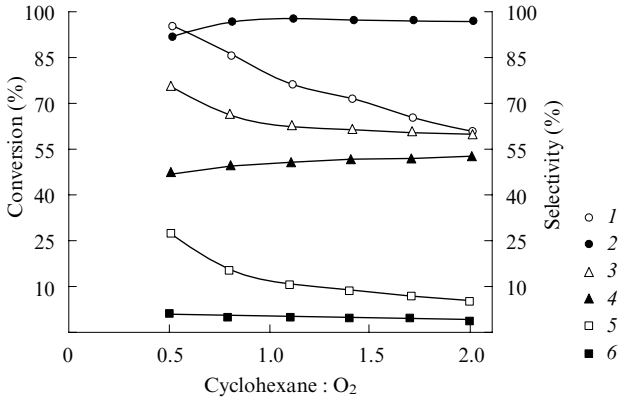


Figure 49. Cyclohexane and O_2 conversion and product selectivities in oxycracking *vs.* cyclohexane : O_2 ratio at 750 °C and reactant flow rate 120 ml min^{-1}.[76]
Conversion: C_6H_{12} (*1*), O_2 (*2*); yields: CO + alkenes (*3*), alkenes (*4*), CO (*5*), CO_2 (*6*).

The cyclohexane : O_2 ratio has a considerable influence on the cyclohexane conversion, which decreases from 96% at cyclo-C_6H_{12} : O_2 = 0.5 to 62% at cyclo-C_6H_{12} : O_2 = 2.0. However, this affects only slightly the selectivity of formation of alkenes and benzene, which remains at 7%, and of CO_2 (< 1%). According to thermodynamic calculations,[76] the autothermal process is possible at cyclohexane : O_2 ratios from 0.69 to 0.80; therefore, the latter value was chosen to carry out most of experiments in this study.

When cyclohexane : O_2 = 0.8, the change of reactant flow rate from 60 to 180 ml min^{-1} at 750 and 850 °C had little influence on the reactant conversion and product yields. When cyclohexane : O_2 = 2.0, *i.e.*, the oxygen concentration is lower, this influence is more pronounced. The effect of reactant dilution with nitrogen in concentration varying from 5% to 75% was also studied. However, no marked influence of dilution on the cyclohexane oxycracking was noted.[76]

The considerable differences between the oxycracking and pyrolysis of cyclohexane are determined by the difference between the initial initiation steps of these reactions. Whereas the initial step of pyrolysis is thermal cleavage of the C–H bond

$$\text{cyclo-}C_6H_{12} \longrightarrow C_6H_{11}^{\bullet} + H^{\bullet}$$

with an activation energy of 433.9 kJ mol^{-1}, the initial step of cyclohexane oxycracking, as in the case of oxypyrolysis of other hydrocarbons, is elimination of the H atom by an oxygen molecule

$$\text{cyclo-}C_6H_{12} + O_2 \longrightarrow C_6H_{11}^{\bullet} + HO_2^{\bullet}$$

with a much lower activation energy (227.2 kJ mol^{-1}).[77] As a result, the difference between the rates of the initial steps can reach several orders of magnitude. However, as it was noted,[76] the role of oxygen in the oxycracking of cyclohexane is not reduced to increasing the initiation rate and increasing the radical concentration. The appearance of oxygen-containing radicals in the presence of oxygen considerably affects the whole mechanism of the reaction and the formation of products. In this respect, the oxycracking of cyclohexane differs substantially from the oxycracking of lighter linear alkanes where the role of oxygen in the formation of pyrolysis products (except for CO and H_2O) is much less pronounced.

Apart from the higher reaction rate and higher yields of more valuable products, two more important advantages of oxycracking were noted.[76] The first one is much lower emission of CO_2. In the thermal pyrolysis, 15%–18% of the initial feed is usually oxidized to CO_2 and H_2O to maintain high temperature. In oxycracking, the oxidation of hydrogen is the main source of heat, and about half of the consumed oxygen is spent for this purpose, while the other half is spent for the formation of CO, so that the CO : H_2O ratio is close to 1, while the yield of CO_2 is an order of magnitude lower. Second, the presence of oxygen eliminates the grave problem of soot formation. In the oxycracking of cyclohexane, no soot deposition on the walls was observed after successive series of experiments.

Faravelli *et al.*[28] compared the experimental data on the partial oxidation of n-pentane, n-hexane and cyclohexane under flow conditions at millisecond contact times with a supported Pt catalyst at temperatures of 1000–1200 K with the results of modelling in terms of gas-phase kinetic model[78] comprising 150 species and more than 3000 elementary reactions (Fig. 50). The model describes well the yield of alkenes; from this, it was concluded that they are mainly formed in the gas phase. At temperature > 1100 K where the selectivity of CO formation is higher than the selectivity of CO_2 formation, the process is mainly homogeneous, although heterogeneous reactions are also involved in the maintenance of radical concentrations. However, at low temperatures (great alkane : oxygen ratios), the conversion and the yield of CO_2 deviate from the model prediction, which attests to mainly catalytic process mechanism under these conditions.

A comparative analysis of the partial oxidation of C_1–C_5 alkanes under flow conditions at short contact times with a Pt gauze with addition of 10% Rh was carried out.[51] Unlike lighter alkanes, when butane and pentane undergo partial oxidation, the increase in the alkane : O_2 ratio and decrease in the yield of alkenes lead to increase in the yield of oxygenates (Fig. 51); in the oxidation of

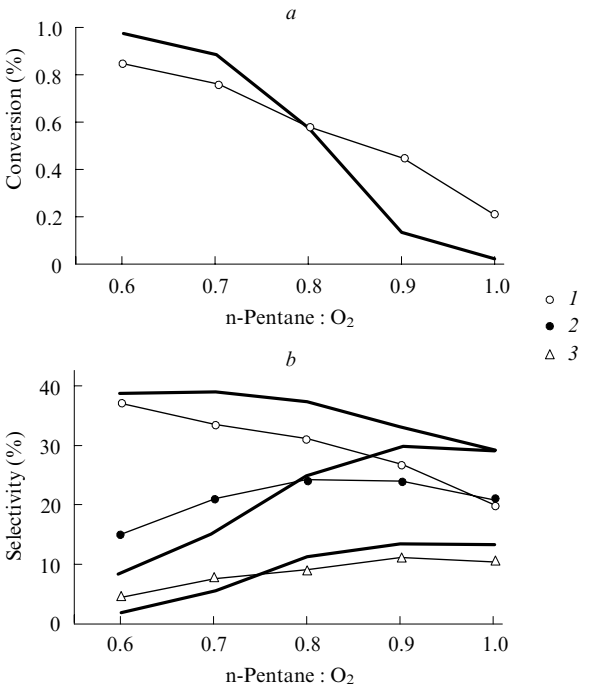


Figure 50. n-Pentane conversion (*a*) and selectivity towards alkenes (*b*) *vs.* n-pentane : O_2 ratio.[28]
Dots denote experimental values, bold lines correspond to calculations; (*1*) ethylene, (*2*) propylene, (*3*) butylene.

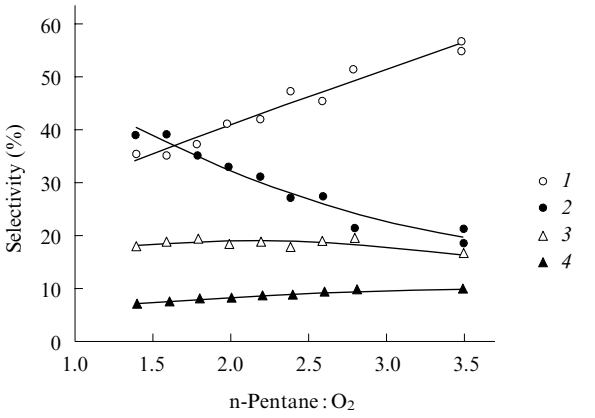


Figure 51. Selectivity of product formation in the partial oxidation of n-pentane *vs.* n-pentane : O_2 ratio on short time catalysis by Pt – 10% Rh gauze.[51]
(*1*) Oxygenates, (*2*) alkenes, (*3*) CO + CO_2, (*4*) alkanes.

n-pentane at n-pentane : O_2 > 1.7, the oxygenate selectivity became higher than the selectivity towards alkenes and reached 60%. The coarser mesh catalyst gauze provides a higher yield of oxygenates, which attests to the gas-phase character of their formation. Acetaldehyde was the major oxygenate, the selectivity of its formation reached 27%; propionaldehyde was the second major product (selectivity of up to 18%). In addition, formaldehyde, methanol, acetic acid, acrolein and ethanol were formed; but the selectivity of each of these products did not exceed 5%.

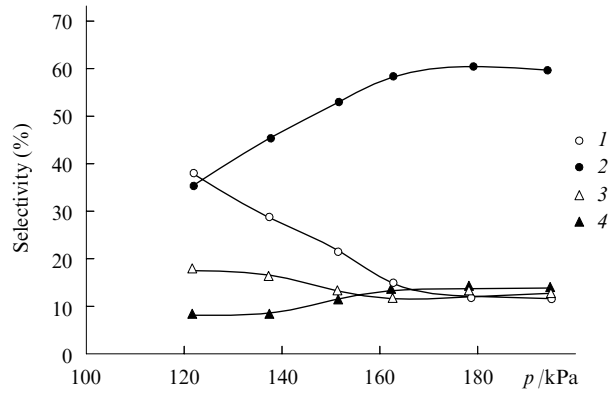


Figure 52. Selectivity of product formation in the partial oxidation of n-pentane *vs.* pressure on short time catalysis by Pt – 10% Rh gauze.[51]
(*1*) Oxygenates, (*2*) alkenes, (*3*) CO + CO_2, (*4*) alkanes.

Pressure increase affects the conversion of pentane and the selectivity of product formation only up to 160 kPa (Fig. 52). According to the authors,[51] the effect of pressure on the process is a serious reason in favour of its gas-phase mechanism.

Figures 53 and 54 compare the conversions and selectivities towards important groups of products *vs.* the C : O ratio for the $C_3 - C_5$ alkanes. It should be borne in mind that under these autothermal conditions, an increase in the C : O ratio entails a sharp decrease in the reactor temperature, which is the main reason for decreasing conversion. The sharp decline for propane and butane is caused by damping of the reaction as it moves out of the autothermal mode. Nevertheless, the difference between the oxidation of pentane and lighter alkanes is quite obvious.

It was shown[79] that the propylene yield in the cool-flame oxidation of pentane (p = 1 atm, T = 723 – 823 K) is almost twice as high as the yield in thermal pyrolysis; however, simultaneously, the ethylene content decreases. By using a milder cool-flame regime, it is possible to reduce the formation of methane twofold and even more. In addition, the oxidation gives rise to oxygenates such as

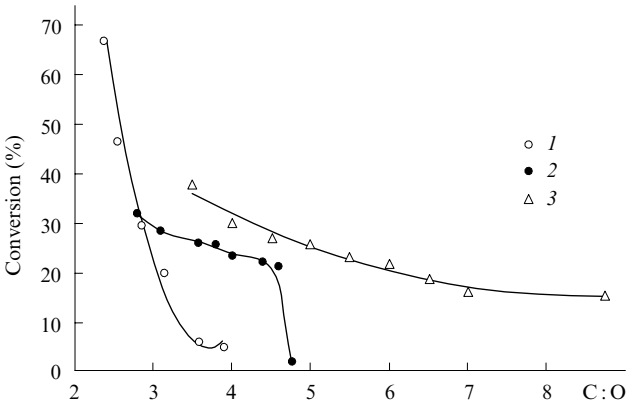


Figure 53. Conversion of $C_3 - C_5$ alkanes *vs.* C : O ratio on short time catalysis by Pt – 10% Rh gauze.[51]
(*1*) Propane, (*2*) n-butane, (*3*) n-pentane.

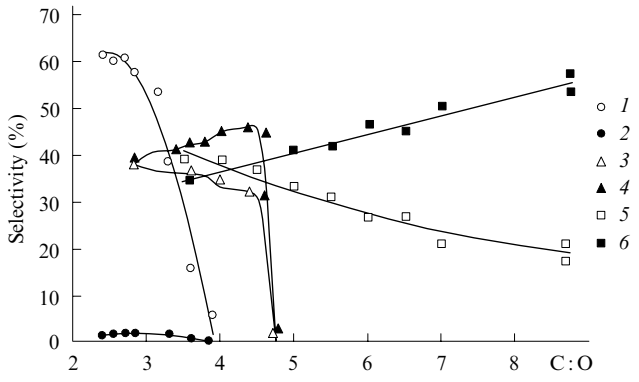


Figure 54. Selectivity of product formation in the partial oxidation of C_3-C_5 alkanes *vs.* C:O ratio on short time catalysis by Pt–10% Rh gauze (40 mesh).[51]
Oxidation products of propane (*1*, *2*), n-butane (*3*, *4*), n-pentane (*5*, *6*); (*1*, *3*, *5*) alkenes, (*2*, *4*, *6*) oxygenates.

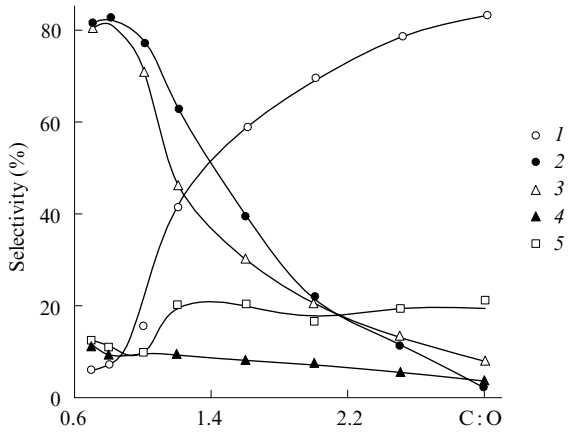


Figure 56. Selectivity of product formation *vs.* C:O ratio in the partial oxidation of n-hexadecane.[59]
(*1*) Alkenes, (*2*) H_2, (*3*) CO, (*4*) CO_2, (*5*) H_2O.

methanol and acetaldehyde. One of the advantages is the absence of soot formation in the reaction zone. When the process is carried out at a temperature of >730 K, a slight resinification occurs after the reactor zone where the temperature does not exceed 600 K, which allows the resin to be removed and subjected to appropriate treatment without process shutdown. However, the soot formation requires rather long contact time ($\sim 5-6$ s), which is an order of magnitude longer than the time of thermal pyrolysis.

A series of studies of the oxycracking of heavier hydrocarbons were carried out. For millisecond contact times and monolith-supported Rh catalyst, partial oxidation of decane, hexadecane and diesel fuel was studied.[59] As the oxygen feed concentration was reduced, along with synthesis gas, alkenes were formed with high selectivity, ranging from ethylene to heavy α-alkenes (Fig. 55), their overall selectivity being up to 80% (Fig. 56). Thus, as the C:O ratio increases, burning to give deep oxidation products (CO_2 and H_2O) switches to reforming giving synthesis gas (CO and H_2) and then to dehydrogenation giving mainly alkenes. The increase in the C:O ratio induces transition from the formation of ethylene to heavier alkenes, exclusively with the terminal double bond. Almost no light alkanes are formed (their overall selectivity is $<8\%$), and they are represented almost exclusively by methane (95%). The alkane conversion and the selectivity of alkene formation increase with increasing molecular mass of the initial alkane. Although it is difficult to elucidate the roles of heterogeneous and homogeneous reactions in this process, the authors believe that CO_2 and CO are mainly formed on the catalyst, while alkenes are produced in gas-phase pyrolysis reactions.

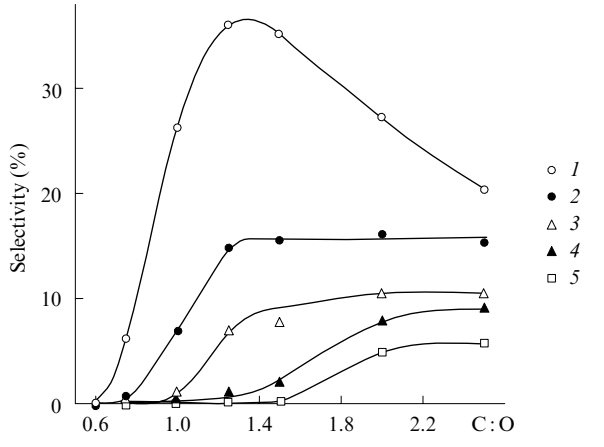


Figure 55. Selectivity of ethylene (*1*), propylene (*2*) and α-alkene (*3–5*) formation *vs.* C:O ratio in the partial oxidation of n-decane.[59]
(*3*) α-Butene, (*4*) α-pentene, (*5*) α-hexene.

An experimental and kinetic investigation of the partial oxidation of n-hexane and n-dodecane was performed to determine the combination of the temperature and the reaction time where solid soot starts to be deposited.[80] These hydrocarbons were chosen as the model diesel fuel which is considered as the source of hydrogen for solid oxide fuel cells (SOFC). Actually, the conditions of ethylene formation were investigated, as ethylene was regarded as the precursor of soot in the reaction of the mixture with the catalyst. According to the results of modelling of various conditions ranging from steam reforming to the catalytic partial oxidation, in a thoroughly stirred mixture at 800 K, a noticeable amount of ethylene is already formed when the reaction time is ~ 0.1 s.

The steam reforming of heptane as a model liquid hydrocarbon in a fluidized-bed membrane reactor (FBMR), with $Pd_{77}Ag_{23}$ membranes meant for selective removal of the hydrogen formed and for shifting the equilibrium, showed a high yield of hydrogen (14.7 moles of H_2 per mole of heptane) at moderate temperature (475–550 °C).[81]

The oxycracking of decalin and tetralin was studied.[82] In the absence of oxygen below 650 °C, almost no pyrolysis of these compounds was observed. In the presence of oxygen, it started at temperatures below 400 °C, and at 650 °C, it reached almost 100%. The major products were lower alkanes and light fuel components. The conversion of oxygen was almost 100% at all of the temperatures studied.

Extensive research is carried out for using physical methods of treatment, mainly various types of electric discharge and plasma to initiate decomposition and oxidation of hydrocarbons as an alternative to their thermal pyrolysis (see, for example, section 11-5 in Ref. 5). However, except for the preparation of such products as acetylene and synthesis gas, the energetic and correspondingly economic cost of application of gas-discharge and plasmochemical technologies for the conversion of natural gas hydrocarbons remains inadmissibly high, especially considering the real efficiency of conversion of the supplied primary power to high-grade discharge energy.

As a typical example, consider the action of barrier discharge on the n-hexane vapour in helium,[83] which results in the formation of compounds with a greater molecular mass than that of the initial molecule, more than a half (70.03%) being the dimer of the starting compound. The reaction products were found to contain no polymers or resinous substances, which is due to the lack of conditions for their formation in the reactor design used where the hydrocarbon film on the cooled reactor walls efficiently removes the reaction products from the area affected by the discharge, thus preventing their subsequent transformation. The impact of the barrier discharge on n-hexane vapour leads mainly to branched hydrocarbons (93.48 mass %). It appears that the most probable mechanism of formation of these products is recombination of the hydrocarbon radicals arising under the action of the discharge.

Products	Content (mass %)
Isooctanes	1.62
Isononanes	17.86
Isodecanes	8.03
n-Decane	2.43
Isododecanes	65.97
n-Dodecane	4.06

The product composition suggests that major radicals formed under these conditions are atomic hydrogen and the hexyl radical. The presence of C_8-C_{10} hydrocarbons in the reaction products indicates that the C—C bonds of the hexane molecule cleave to give radicals with fewer carbon atoms than present in the initial molecule. The substantial fraction of nonanes means that cleavage of the C—C bonds affords mainly propyl radicals. Therefore, the formation of C_9 and C_{12} hydrocarbons can be described by the following reaction sequence (He* are metastable helium atoms):[83]

$$C_6H_{14} \xrightarrow{e,\ He^*} C_6H_{13}^{\bullet} + H^{\bullet}$$

$$C_6H_{14} \xrightarrow{e,\ He^*} 2\,C_3H_7^{\bullet}$$

$$2\,C_6H_{13}^{\bullet} \longrightarrow C_{12}H_{26}$$

$$C_6H_{13}^{\bullet} + C_3H_7^{\bullet} \longrightarrow C_9H_{20}$$

In addition to experimental studies, adequate kinetic models of oxypyrolysis of single alkanes starting from methane and up to petrol and diesel hydrocarbons are being actively developed. The un-to-date level of understanding of the kinetics of radical-chain oxidation of light alkanes at moderate temperatures (300–1000 °C) prompts that oxypyrolysis of C_1-C_6 alkanes can be described as a special case of a more general class of homogeneous-heterogeneous partial oxidation of alkanes in the medium temperature range in terms of a common kinetic mechanism.[5] Currently, various research groups are actively engaged in the design of such models and gradual extension of the scope of their application to the whole set of light alkanes.[9–13]

For inclusion of the alkane oxidation kinetics into complex gas-dynamic processes, so-called 'skeletal' or 'global' mechanisms are widely used. Despite the obvious roughness of this approach, with the potential of computing means at hand, this approach is suitable for taking into account the heat evolution dynamics and the yields of most important products. For example, this mechanism was applied to study low-temperature ignition of n-butane.[13] Attempts are also made at the analytical description of the conversion of alkanes. A general expression for the conversion rate (in kmol m^{-3} s^{-1}) of normal alkanes that are heavier than pentane was proposed [28]

$$r = 3\times 10^{12}(n_C-3)^{0.5}(n_C-1)\exp\left(-\frac{50500}{RT}\right)\times$$

$$\times\, C_{hyd}\left[1+1.2\,C_{O_2}^{0.33}\exp\left(-\frac{6500}{RT}\right)\right],$$

where n_C is the number of carbon atoms in the hydrocarbon, C_{hyd} and C_{O_2} are the hydrocarbon and oxygen concentrations. This expression does not take into account the presence of an induction period but provides a satisfactory agreement with the predictions of the detailed kinetic scheme for 60% conversion of the hydrocarbon.

V. Conclusion

Owing to its characteristics, the oxidative pyrolysis of alkanes remains an attractive subject for industrial implementation, as indicated by high research activity in this field, although there are no large operating plants (except for methane oxypyrolysis). However, to draw the attention of petrochemical industry to new processes based on oxypyrolysis, it is necessary to convincingly demonstrate a perceptible economic benefit. Currently, rather stringent requirements are imposed on the selectivity of alkene production processes. According to the available economic estimates for currently existing prices, to achieve only the break-even point for the catalytic oxidative cracking of light alkanes and naphtha, the overall selectivity towards C_2-C_4 alkenes should exceed 63% (Fig. 57). Although the catalytic oxidative cracking is much more effective than pyrolysis as regards the required power supply, this is too little. Despite the technical feasibility, due to greater feedstock consumption (as some of the feed must be spent for attaining the required temperature), catalytic oxidative cracking still appears not very attractive from the economic standpoint as compared with pyrolysis.[73]

However, the scope of possible applications of light alkane oxypyrolysis is not limited to the synthesis of alkenes. In addition to the well-mastered acetylene and technical carbon production processes, note the application for increasing the quality of motor fuels, which is long

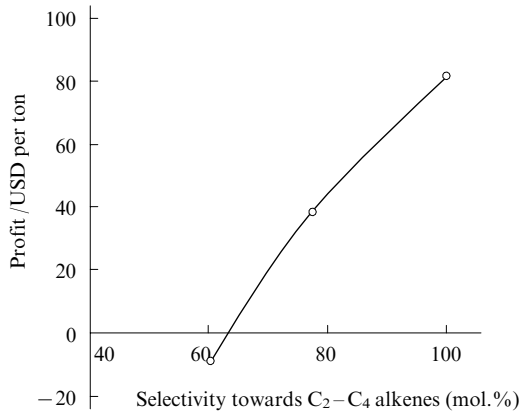


Figure 57. Profitability of alkene production by naphtha catalytic oxidative cracking *vs.* selectivity of alkene formation.[73]

known, although seldom mentioned lately.[84] Recent studies[74] demonstrated good prospects of selective oxypyrolysis of C_{5+} alkanes in associated gas to be used as efficient fuel for gas-piston and gas-turbine power plants. It was shown that the yield of light products can be increased by activating the residual asphalt thermal cracking by air oxygen.[85]

New prospects for the practical implementation of gas-phase processes based on oxypyrolysis are opened up due to the rapidly growing demand in relatively simple, flexible and low-tonnage gas chemical units for processing and transportation of non-conventional hydrocarbon gas resources (marginal and low pressure fields, shale gas, coal-bed methane, associated gas, *etc.*).[86, 87] However, wide practical use of processes based on the oxypyrolysis of light alkanes is hardly possible without the knowledge of their mechanism. Therefore, much work is to be done to study the oxidation kinetics of single alkanes and their complex mixtures corresponding to real natural and associated gas and its dependence on the key process parameters. Up to now, the vast majority of investigations have been carried out under atmospheric pressure, and little information is available on the processes performed at elevated pressure, which are most interesting for commercialization. There are almost no data on the mutual influence of light alkanes with appreciably different reactivities during their joint oxidation.

The in-depth understanding of the kinetics of complex non-linear reactions involved in alkane oxypyrolysis is impossible without adequate kinetic modelling. A number of models have already been proposed in the literature, but all of them require thorough verification against available experimental data, which have been just systematized and analyzed in this review for the subsequent correlation with the results of kinetic modelling.

The authors hope that the presented information would be helpful for more profound understanding of the mechanism of the oxidative conversion of light alkanes and for progress in the development of the industrial processes using these reactions.

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