



Editor's choice paper

The interplay of catalytic and gas-phase stages at oxidative conversion of methane: A review

Vladimir S. Arutyunov^{a,b,*}, Ludmila N. Strekova^b^a Institute of Problems of Chemical Physics, Russian Academy of Sciences, av. Semenova 1, Chernogolovka, Moscow Region, 142432, Russia^b Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow 119991, Russia

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ABSTRACT

The effective functionalization of C–H bond in methane, the main hydrocarbon component in Earth's crust and the most real source of energy for mankind in the nearest observable future, is undoubtedly can be regarded nowadays as one of the most important scientific and technological tasks. However, the usual practice of considering catalytic and gas-phase processes as independent technological branches seriously restricts the possibilities for a deeper understanding and technological optimization of real processes. The development of more effective technologies to convert methane and other gas-phase hydrocarbons into more valuable and demanded chemicals needs a complex approach based on the combined heterogeneous–homogeneous chemistry of these processes. A number of examples are used to illustrate the interconnection between heterogeneous catalytic and gas-phase processes in oxidative functionalization of methane. A number of potential possibilities for the optimization of the real heterogeneous–homogeneous chemistry of these processes are discussed.

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1. Introduction

The effective and inexpensive conversion of methane, the principal component of natural gas, into more valuable and demanded chemicals is a long-sought goal not only for relatively young gas chemistry, but also for organic chemistry as a whole. Search for appropriate solutions of this task continues for more than a century. Nevertheless, the global significance of its successful solution has become particularly evident only recently, after it had been established that the overwhelming majority of hydrocarbons in the Earth's crust, that is global future energy and petrochemical resource of mankind, is presented by different kinds of gas-phase hydrocarbons [1].

The permanent decrease of available liquid hydrocarbons resources, which are undoubtedly the most attractive and convenient stuff for use and processing, makes the transition of the world economy to gas-phase stuff, namely methane, inevitable. Today, at the beginning of the new century it is evident that the 21st century

will be the century of natural gas, and as a consequence, the century of gas chemistry. A significant decrease in the gas price relative to that of oil makes natural gas very attractive not only as a fuel, but also as a petrochemical raw material. That is why a very high activity in developing new gas chemical enterprises is observed, particularly in the USA and Middle East, two regions with huge resources of inexpensive shale or natural gas.

Many new gas chemical plants were announced to use as a raw stock ethane and heavier hydrocarbons extracted from natural gas. However, the production of olefins by dehydration of ethane and its heavier homologues, which constitute only a minor part of natural gas, is an established industrial-scale petrochemical process. A more ambitious goal for gas chemistry is to build a methane-based analog of petrochemistry.

Note, however, that methane-based gas chemistry defers fundamentally from traditional “destructive” petrochemistry by its “constructive” trend, with the aim to produce from CH₄, the most simple and stable hydrocarbon molecule, a variety of more complex and less stable products that are now produced by petrochemistry. This task is difficult to realize because methane is a low-reactive hydrocarbon, with a thermodynamic stability exceeding not only that of all other hydrocarbons, but also that of the majority of target chemicals to produce from it.

Traditionally, the overwhelming part of industrial methane processing is based on high-temperature heterogeneous catal-

* Corresponding author at: Institute of Problems of Chemical Physics, Russian Academy of Sciences, av. Semenova 1, Chernogolovka, Moscow Region, 142432, Russia.

E-mail addresses: v.arutyunov@mail.ru, arutyunov@chph.ras.ru (V.S. Arutyunov), strekova@bk.ru (L.N. Strekova).

ysis [2,3]. Despite of intense attempts to develop appropriate low-temperature homogeneous catalytic systems and numerous excellent researches in this field describing new trends in oxidative functionalization of C–H bonds [4–12], at present they can hardly be considered as a real base for industrial applications and show “concepts rather than recipes” [10]. The possibility of using for this purpose homogeneous gas-phase processes of direct conversion of methane into methanol or ethylene, although intensively investigated [2,3,13–18], has only limited scope of practical applications. The same applies to the halogenation of methane. That is why the analysis of the most promising ways for the industrial-scale functionalization of the C–H bond in methane, as well the mechanisms of these processes and possibilities of their optimization, remain one of the most important practical tasks.

In relation with this task, it is necessary to highlight one very important peculiarity of the high-temperature heterogeneous catalytic processing of methane: in most cases, it involves hetero-phase processes that take place in conditions of an intense competition between catalytic and parallel gas-phase reactions. This situation was clearly elucidated by investigations of the oxidative coupling of methane (OCM), for which the heterogeneous generation of methyl radicals and their subsequent homogeneous gas-phase reactions constitute a combined indivisible mechanism [19].

Unfortunately, until recently researchers working in catalysis and gas-phase chemistry had applied very different methodologies to solving their problems. Therefore, it is desirable to bridge this gap. The practical realization and optimization of catalytic processes of methane conversion and an active control of it require detailed information on the interaction between catalytic and gas-phase stages of these complex radical processes. Only an optimal coupling of catalytic and gas-phase chemistry can provide the best use of the advantages of both: a combination of a high rate and high selectivity of catalytic activation with a high productivity and technological simplicity of homogeneous gas-phase processes.

The aim of this review is to attract the attention to very important and interesting problem of the interplay between the heterogeneous and homogeneous stages of the catalytic activation of methane and demonstrate the most interesting examples and emerging possibilities. It was done mainly by the examples of the well known processes of oxidative Direct conversion of Methane To Methanol (DMTM) and Oxidative Coupling of Methane (OCM) to ethane and ethylene.

2. On the interaction between the catalytic and gas-phase stages of methane oxidation

The oxidative activation of methane is one of the most evident and energy effective methods of its activation, which involves only a small external energy input. Outside the production of halogenated derivatives of methane, the practical application of which are now restricted for the well-known reasons, the oxidative activation of methane can be considered as the main method for its activation with subsequent conversion into various chemicals. Firstly, the oxidative conversion makes it possible to convert methane to syngas, one of a few products obtainable from it through a thermodynamically equilibrium process. Only after this step, it is possible to obtain from methane a variety of basic products, such as hydrogen, ammonia, methanol, synthetic liquid hydrocarbons, etc., which, in turn, serve as semi-products for many different chemicals.

The existing processes of oxidative conversion of natural gas, including its conversion to syngas, are largely catalytic. However, these catalytic processes have features that significantly distinguish them from other catalytic processes. The very high energy of the C–H bond of the methane molecule, 104 kcal/mol, explains why

relatively high temperatures, typically above 400 °C, are needed even for the catalytic oxidation of methane. Such temperatures ensure that not only catalytic but also gas-phase processes involving various less stable intermediates formed by catalytic activation and subsequent oxidation of methane proceed at high rates. Thus, the specificity of these processes is that they are, in fact, hetero-phase processes occurring under conditions of intense competition between heterogeneous and concurrent gas-phase reactions. This has become especially clear from studies of the oxidative coupling of methane, a process in which the heterogeneous reactions of initiation of methyl radicals and their subsequent homogeneous transformation comprise a single integrated mechanism [19].

In the presence of oxide catalysts, the known reactions of methane oxidative conversion have a number of common features, which suggests that their first and rate-limiting step is the interaction of CH₄ with the catalyst surface to form CH₃• radicals, capable of escaping into the volume of the reactor. This assumption was confirmed by direct experimental observations of methyl radicals release from the catalyst surface, estimates of the rate of their catalytic production, and data on the role of the gas phase in these processes. Thus, in reality, they are multistage heterogeneous-homogeneous processes occurring in part on the surface of catalyst and in part in the gas phase. Moreover, as it was demonstrated by a comparison of experimental data and the results of kinetic modeling of the oxidative coupling of methane [20,21], the role of the catalyst in these reactions is apparently limited mainly to the generation of methyl radicals.

Catalytic reactions of methane reforming to syngas, oxidative coupling of methane to ethane and ethylene, direct oxidation of methane to methanol and formaldehyde occur at relatively high temperatures, 400–1000 °C, i.e., can be qualified as high-temperature catalytic oxidation processes. Numerous studies of these reactions, different in many ways, showed, however, that they have a number of common features, the most important of which are:

- (I) High and similar activation energies (~200 kJ/mol);
- (II) The proportionality of the reaction rate to the methane partial pressure,

$$w = kP_{\text{CH}_4}; \quad (1)$$

- The weak dependence of the reaction rate, if any, on the partial pressure of oxygen;
- The manifestation of the kinetic isotope effect of the reaction rate (in most cases, $k_{\text{CH}_4}/k_{\text{CD}_4} > 1$);
- A limited output of products (with the exception of complete oxidation and conversion to syngas).

For example, the catalytic oxidation of methane to methanol is characterized by a very low yield. At atmospheric pressure, a typical methanol yield is 0.5–1.5%. Even at a pressure of up to 5 MPa, close to the pressure of the gas-phase oxidation of methane to methanol, the maximum yield on the best catalysts (Fe–Na–sodalite and ferri-silicate) is 4% at 410–430 °C. For the catalytic oxidation of methane to formaldehyde, the maximum yield is higher, 2–4%. The best catalyst for this process is evidently V₂O₅/SiO₂, which enables to obtain such yields at 550–600 °C. The activation energy of this process on the MoO₃/SiO₂ catalyst is 189 kJ/mol. Much higher yields reported for these two processes have not been confirmed in later publications. In the majority of the studies, the kinetics of these reactions obeys Eq. (1) [21].

The data on the kinetics of the oxidative condensation of methane are more numerous than on the other reactions of its oxidation. They show that the yield of C₂ hydrocarbons in this reaction does not exceed 25%. As for the aforementioned processes, reports

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