Free radicals in catalytic oxidation of light alkanes: kinetic and thermochemical aspects

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Abstract

The kinetic and thermochemical analyses of the catalytic oxidation of C_1–C_4 alkanes indicate that the overall reaction network includes both homogeneous and heterogeneous elementary reactions of free radicals. Two thermochemical parameters of oxide catalysts, the affinity of the surface active site $E_{[O–H]}$ to a hydrogen atom and oxygen binding energy $E_{[O]}$, are the main factors determining the kinetic features of the overall process. The possible contribution of free radical reactions to some metal-catalyzed processes (steam reforming, partial and total oxidation of methane) is analyzed. Trends in the studies of catalytic chemistry of free radicals and in the development of innovative catalytic processes of light alkane transformation into valuable products are discussed.
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1. Introduction

Recent developments in heterogeneous catalysis present numerous examples of the interplay between the practical industrial needs and advances in the mechanistic studies of catalytic reactions. For instance, the petroleum crisis of the late 1970s shifted an interest from olefins to light alkanes as initial compounds in the chemical industry. As a result, peculiar features of alkane chemistry and reactivity became the focus. In particular, a revival of a considerable interest in the so-called heterogeneous–homogeneous processes and heterogeneous reactions of free radicals had appeared.

The heterogeneous reactions of free radicals were initially considered as termination steps in chain processes (see, for instance [1–3]). A possible role of such reactions in initiation [3,4] and propagation [5] of chains has also been discussed. More recently, the possibility of homogeneous reactions accompanying heterogeneous catalytic processes has been demonstrated [6–8]. Although the idea of heterogeneous–homogeneous processes [9,10] implied that such processes include steps localized both in a gas phase and on any surface (reactor walls, "inert" reactor packing materials, and active catalysts), their contribution was considered marginal in most catalytic transformations of hydrocarbons. However, in the early 1980s, the oxidative coupling of methane (OCM) was discovered [11–15], and it was shown that the first OCM product, ethane, forms via the recombination of free methyl radicals, which escape into the gas upon methane molecule interaction with surface active sites [16–18]. In other words, the formation of free radicals and their further transformation is the major and essential reaction pathway, which determines the main features of the overall process and product distributions.

As exemplified by the OCM process, the new family of catalytic reactions requires special approaches to mechanistic studies and the use of methods originally developed in homogeneous gas phase kinetics based on the techniques that enable the measurement of concentrations of free radicals in the course of a catalytic reaction. Advantages and limitations of such methods are discussed in review papers (see, for instance [19–22]). At this point, it should be mentioned that either the presence of free radicals or their apparent absence in the reaction mixture under certain reaction conditions becomes significant only by being analyzed in the framework of distinct notions of the process under study. This paper demonstrates how such notions can be elaborated by combining the thermochemical and kinetic analyses of light alkane catalytic oxidation. Among others, the emphasis will be on two related processes: OCM and oxidative dehydrogenation (ODH) of C_2–C_4 alkanes.

Table 1
Possible processes of alkane molecule activation

Type of activation process	Chemical equations		Expression for E_{ex}
(i) Homolytic dissociation of C–H bonds	$[O] + RH \rightarrow [OH] + R$	(1)	D_{R-H}
(ii) Heterolytic proton abstraction form C–H bond on a strong basic center	$[O^{2-}] + RH \rightarrow [O^{2-}\cdots H^+] + R^-$	(2)	$D_{R-H} + I_{H-} - I_{R-}$
(iii) Heterolytic hydride ion abstraction from C–H bond on a Lewis acidic site	$[M^{n+}] + RH \rightarrow [M^{n+}\cdots H^-] + R^+$	(3)	$D_{R-H} + I_{R-} - I_{H-}$
(iv) Ionization of alkane molecule	$[h^+] + RH \rightarrow [h^+\cdots e^-] + RH^+$	(4)	I_{RH}
(v) Synchronous abstraction of two hydrogen atoms	$M^{n+}\cdots O^{2-} + C_nH_{2n+2}$		$\Delta H_f(ol) - \Delta H_f(al)$ (lower limit)
	$\rightarrow [M^{n+}\cdots H^{\delta-}\cdots C_nH_{2n}\cdots H^{\delta+}\cdots O^{2-}]$		
	$\rightarrow M^{n+}\cdots O^{2-} + C_nH_{2n} + H_2$ or	(5a)	
	$\rightarrow M^{(n-2)+}\cdots[\,] + C_nH_{2n} + H_2O$	(5b)	

[O], strong oxidizing surface center having a high affinity to the hydrogen atom; [h$^+$], hole center; [h$^+\cdots$e$^-$], trapped electron; D_i, energy of homolytic dissociation of corresponding bond; I_i, ionization potentials of corresponding particles; $\Delta H_f(i)$, enthalpies of formation of corresponding substance.

2. Activation of alkane molecules—thermochemistry

Since alkane molecules have no specific "reactive centers" such as functional groups or multiple bonds, they can be activated only via bond dissociation or charge transfer. The more energetically favorable the activation process, the higher the probability of its contribution to the overall reaction. The feasibility of activation processes can be estimated based on the value of the energy expenditure E_{ex}

$$E_{ex} = \Delta H - E_{st}, \qquad (I)$$

where ΔH is the overall enthalpy change and E_{st} is the energy of stabilization of an activated molecule (fragment) on the surface.

According to Eq. (I), the overall enthalpy change (ΔH) is an algebraic sum of two terms: the energy that should be consumed for alkane molecule activation (E_{ex}) and the exothermic effect of the interaction of activated molecule or its fragment(s) interaction with the catalyst surface (E_{st}). Possible activation processes and the corresponding expressions for E_{ex} are presented in Table 1. Here the same numbering of reactions as in Table 1 is used. The values of E_{ex} calculated from available thermochemical data [23] and presented in Table 2 show that the energy of stabilization E_{st} required to compensate for E_{ex} is minimal

for the homolytic C–H bond dissociation process (1). On the other hand, one may assume that the energy of the O–H bond formed in this process is comparable to E_{ex} and it may be unnecessary to bind the second fragment (free radical R) to the surface to compensate for the energy of C–H bond breaking. This assumption agrees well with direct calorimetric measurements: in the case of oxide catalysts active in OCM and in ethane ODH [24,25], as well as in total oxidation of alkanes [26], the O–H bond strength ranges from 250 to 470 kJ mol^{-1}.

On the contrary, in the case of the heterolytic C–H bond dissociation, the E_{ex} value is so large that its compensation requires the binding of both fragments to occur in a single step. This can only take place in the presence of paired centers with specific configurations and energy relations. Moreover, since the E_{ex} values for processes (2) and (3) are comparable with the molar lattice energy for stable oxides such as MgO and Al$_2$O$_3$, it is highly unlikely that these paired centers can survive in the presence of such active components of the reaction mixture as water and CO$_2$. For a similar reason, the probability of process (4) is low, since it requires the existence of stable hole centers with electron affinities comparable to the ionization potentials of light alkane molecules ranging between 9 and 13 eV [23] and

Table 2
Energy expenditure on the activation of light alkane molecules

Molecule	Energy expenditure, kJ mol^{-1}				
	Reaction (1)	Reaction (2)	Reaction (3)	Reaction (4)	Reaction (5)
CH$_4$	431	1630	1308	1250	–
C$_2$H$_6$	410	1615	1183	1120	(137)
C$_3$H$_8$	398	1609	1162	1078	(124)
n-C$_4$H$_{10}$	393	1605	1154	1037	(115)
iso-C$_4$H$_{10}$	389	1601	1120	1016	($\sim$117.5)

being higher than the gap width for most of the materials (semiconductors and even insulators).

One more process, which could also be considered as an initial activation step is the so-called "concerted" (synchronous or simultaneous) abstraction of two hydrogen atoms (v), similar to that previously suggested [27] for the first step of n-butane transformation into maleic anhydride over V–P–O catalysts. No simple expression can be written for E_{ex} for process (5a), but the difference between the enthalpies of formation of olefin and initial alkane, $\Delta H_f(ol) - \Delta H_f(al)$, can be taken as a lower limit (given in brackets in Table 2). They indicate that thermochemistry is still a ruling factor. The thermochemistry of process (5b) will depend on the binding energy of active oxygen that is involved in the water formation. One may assume that because of steric constraints, the smaller the alkane molecule, the lower the probability of such a process.

The above analysis shows that free radical formation is likely the most energetically favorable process of light alkane activation. However, this thermochemical argument does not an unambiguously prove the free radical character of any catalytic reaction. In each particular case the specific kinetic evidence is required to prove or disprove it. In the next section the data on the kinetic features of C_2–C_4 alkane ODH are analyzed from this standpoint.

3. Reactions of free radical in the course of catalytic process—kinetic analysis

Currently there are two different approaches to the organization of the ODH process. One has been initiated by the pioneering studies of Schmidt and coworkers [28–30] and assumes that catalysts operate at very short (millisecond) contact times. Such processes proceed autothermally over gauze or monolith catalysts loaded with Pt-group metals or active oxides, i.e., at high temperatures (well above 1200 K) and with high void volume fraction in the reaction zone. It is very probable that catalysts promote the ignition and then the process proceeds predominantly in the gas phase. This concept tends to become prevailing in the literature (see, for instance [31–37]).

In the framework of the second approach, the ODH reaction is carried out in a "traditional" way: in reactors packed with oxide catalysts, typically bulk or supported V- and Mo-containing oxide systems, at temperatures below 1000 K and relatively low flow rates. Kinetic features of such processes are discussed here in more detail. One can recognize two groups of studies devoted to this subject. Although they at first glance seem to lead to contradictory conclusions on the mechanism of ODH process, a more detailed analysis demonstrates that they are complimentary.

First, publications by Stern and Grasselli [38,39] and by Bell and Iglesia with coworkers [40–48] which present extensive analysis of the ODH reaction mechanism over catalysts with varied chemical composition are worth mentioning. This analysis is based on the kinetic and isotopic tracer data and catalyst characterization. Note that in these papers the intrinsic mechanism is described almost exclusively in terms of heterogeneous chemistry and the corresponding kinetic models. On the other hand, some results presented in the literature by several research groups (see, for instance [49–59]) offer a clearer view of how reactor arrangements affect the features of light alkane oxidation over traditional catalytic systems and demonstrate the importance of homogeneous factors in the processes under study.

Table 3 illustrates that these two sets of results reflect different aspects of the overall process. The conditions chosen for kinetic studies in [38–48] (relatively low temperatures, low conversions, and the complete packing of the void volume with "inert" materials) sharply decrease the probability of the homogeneous process development. Then, the observed reaction parameters presumably reflect the sole behavior of surface active sites (or species). Nevertheless, it can be shown that even in the absence of void zones gas phase processes can affect the reaction under study and lead to several unusual effects.

An example of this kind is given in Fig. 1 (using data from [59]): over a series of supported V-containing oxide catalysts the conversion of iso-butane sharply increases with an increase in the particle size at a nearly constant ODH selectivity, which remains close to $28 \pm 1.5\%$ in the case of γ-alumina and varies from 67 to 78% over all V-containing catalysts. The only reasonable explanation of such a behavior is the development of a chain reaction, which becomes more pronounced as linear dimensions of gaps between catalyst particles increase. This is consistent with analysis performed in [60]: if the reaction proceeds via the formation and transformations of free radicals, the contribution of the gas phase to the overall reaction rate (the conversion of reactants) drastically increases when the characteristic size of gas gaps increases from 10^{-2} to 1 mm. This is exactly the range of sizes when one series of samples presented in Fig. 1 switches to the other.

Interestingly, the difference in the hydrocarbon conversions observed over large and small catalyst particles (3.5–17%) is much greater than the conversion that is usually observed in the reactor packed with inert materials (1.3–2.5%) [39,51,56,59]. This fact suggests that the free radical chain reaction initiated by the surface of active ODH catalysts is much more efficient than that occurring in the presence of inert materials which, mostly terminate the process.

In the case of OCM and ODH it is very likely that a serious problem will be faced when trying to extract the intrinsic kinetic constants of elementary heterogeneous interactions from experimental data. The rates of reactant conversion and product formation are a complex combination of terms attributed to numerous elementary reactions localized both on the catalyst surface and in the gas phase. Moreover, if the contribution of homogeneous processes can be minimized, the question arises as to whether and how the resulting rate constants and equations can be used to describe the system

Table 3
Reaction conditions for ODH studies and typical results obtained

Refs. [38–48]	Refs. [49–59]

Reaction conditions

1. Relatively low temperatures (typically—703 K or below; 823 K— in [39])	1. Relatively high temperatures (typically—above 773 K)
2. Low hydrocarbon and oxygen conversions (typically between 2 and 20%) achieved by varying the flow rate and catalyst loading	2. High conversions of reactants (up to nearly total consumption of limiting reactant, as a rule—oxygen)
3. In some cases—diluted with "inert" material (as a rule—quartz chips)	3. Both dilution of catalyst and packing of void spaces before and after the catalyst bed are subjects for the study
4. Packing of the void volume with inert material	

Some results and conclusions

1. Overall ODH is irreversible	1. Homogeneous reaction taking place in the postcatalytic volume increase the yield of olefin in ODH reaction
2. C–H bond activation is a kinetically relevant and irreversible step	2. High ODH selectivity (above 70% [59]) can be achieved at high conversions
3. ODH selectivity decreases with increasing conversion	3. Product distributions are strongly affected by hyodynamic factors and reactor arrangements (including dilution of active catalyst with "inert" materials [55])
4. ODH kinetics is consistent with Mars–van Krevelen redox scheme	
5. Carbon oxides (CO_x) are formed from both alkane and olefin	4. Unusual effect of catalyst particle size is observed (see text and Fig. 1)
6. Alkane transformations into olefins and CO_x involve the same kinetically relevant step	5. Processes over active catalyst and in the void volume (even downstream) are interdependent
7. The same surface sites participate in the activation of alkane C–H bonds (ODH) and olefin C–H bonds (total oxidation)	

behavior under the conditions that allow the optimal yield of a desired product.

It is evident that conventional kinetic models used in heterogeneous catalysis cannot describe the features of a reaction if it proceeds in the gas phase at least partially. Neither can the only use of methods peculiar to homogeneous kinetics be successful. Several attempts have been made (see, for instance [61–67]) to complement the multistep kinetic models of homogeneous oxidation with some heterogeneous steps (as a rule, initiation and/or termination of free radical processes) in constructing the models of such processes. Despite some success of these attempts, this description is far from being perfect. In fact, the total number of surface sites in the presence of a catalyst with a surface area of $1 \text{ m}^2 \text{ g}^{-1}$ is comparable with the number of particles in the gas phase in a unit volume. Accordingly, the number of heterogeneous collisions for any particle is comparable with that in the gas phase. The importance of heterogeneous reactions will further increase with the catalyst surface area. This means that, for each type of reactive particles existing in the gas phase during hydrocarbon oxidation, one should consider all possible types of reactions with surface active sites and include them in the overall kinetic scheme. It is a really complicated problem since neither the rate constants nor even a stoichiometry of heterogeneous interactions of free radicals is usually known.

Fortunately, the chemistry of free radicals involved in the gas phase oxidation of light alkanes and the kinetics of their elementary reactions have been very well studied [68–71]. These data provide a good idea of the main types of radical reactions and their principal features. Based on this information, an approach to the kinetic description of complex heterogeneous–homogeneous catalytic reactions was suggested and applied to the OCM process several years ago [72,73]. This is based on two assumptions:

1. The overall process is a combination of the gas phase reaction with heterogeneous steps of three main types: H- and O-atom transfer and radical capture.
2. The main features of heterogeneous processes over insulators and wide-gap semiconductors are similar to those existing in homogeneous reactions of the same types.
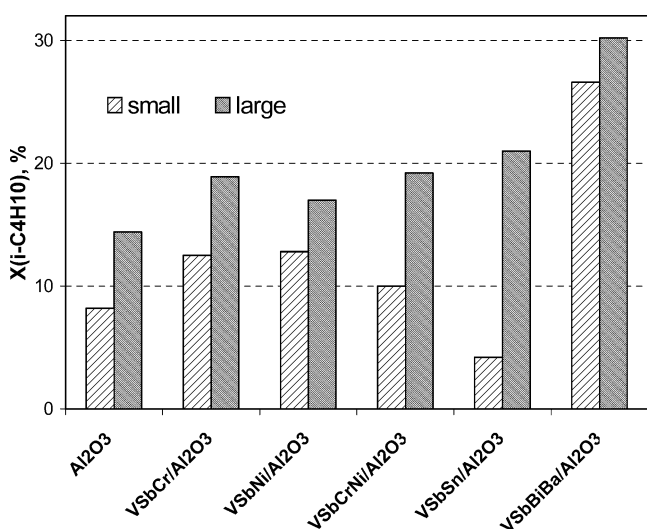

Fig. 1. Conversions of iso-butane at 550 °C over γ-Al_2O_3 and alumina-supported V-containing catalysts of different particle size: 1.8–2.0 mm (large) and 0.3–0.8 mm (small); initial gas mixture—22% i-C_4H_{10} + 12% O_2 in N_2, flow rate 54.5 ml/min, catalyst volume 4 ml, and void volume totally packed with quartz chips.

The former assumption allows one to compose multistep reaction schemes by counting pairwise interactions between gaseous species and surface active sites. The next crucial step is the evaluation of the corresponding rate constants. The latter assumption provides the possibility of evaluating the kinetic parameters for each elementary step. The preexponential factors can be estimated based on the gas surface collision frequencies and steric factors taken by analogy with the corresponding homogeneous reactions. The activation energies E_a can be estimated from the Polanyi–Semenov equation [3]:

$$E_a = a + b * \Delta H. \tag{II}$$

The values of coefficients a and b in Eq. (II) depend on the type of a reaction and on the sign of the reaction enthalpy ΔH [3]. They can be evaluated from data on gas phase reactions of the same type (see, for instance [68–71]). In particular, for reactions of H-atom abstraction from saturated hydrocarbons, $a = 25$–50 kJ/mol; $b \approx 0.75$ and $b \approx 0.25$ for endothermic and exothermic reactions, respectively. To accomplish the evaluation procedure, information on the enthalpies of elementary heterogeneous reactions, i.e., the pertinent data on the catalyst thermochemistry, is required.

4. Thermochemistry of oxide catalysts and kinetics of heterogeneous reactions

The importance of thermochemical information in analyzing the mechanisms of catalytic processes is beyond any question. At the same time, the properties of a solid should refer to its state in the conditions close to those in which the catalytic reaction of interest occurs. Taking this into account, we have developed an in situ calorimetric technique that enables the study of the thermal effects of various processes in heterogeneous gas–solid systems at temperatures of up to 1000 K. The experimental set-up is based on the Setaram DSC-111 calorimetric unit with flow cells and online gas chromatographs; it combines the advantages of transient-response (pulse) techniques with simultaneous quantitative measurements of thermal effects in the conditions of real catalytic processes. The outline of the method and some examples of its application are presented in [25]. Here it is worth noting that this method provides unique information on the surface chemistry and thermochemistry of oxide OCM and ODH catalysts. In particular, it was demonstrated that the strength of the surface O–H bond formed in reaction (1) is the factor that controls the activation of methane and ethane over oxide catalysts: the higher the O–H binding energy $E_{[O–H]}$, the more rapid the reaction between the hydrocarbon molecule and the preoxidized catalyst surface. Moreover, as can be seen from Fig. 2, the relationship between E_a and ΔH for the reaction
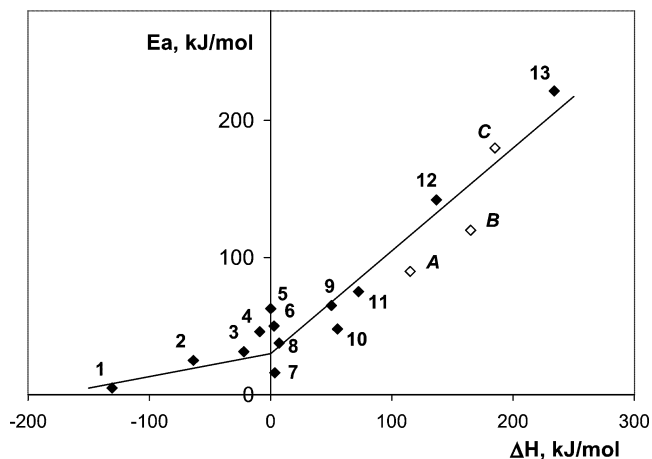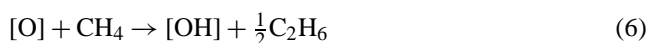
$$[O] + CH_4 \rightarrow [OH] + \tfrac{1}{2}C_2H_6 \tag{6}$$

Fig. 2. Activation energy as a function of enthalpy change for gas-phase reactions of CH_3-radical formation $X + CH_4 \rightarrow XH + CH_3$ and for ethane formation during methane interaction with the OCM catalysts. $X = F$ (1), OH (2), C_6H_5 (3), CF_3 (4), CH_3 (5), H (6), Cl (7), O (8), SH (9), CH_3O (10), Br (11), I (12), O_2 (13). OCM catalysts—Li/MgO (A), K/Al$_2$O$_3$ (B), Pb/ Al$_2$ O$_3$(C).

obeys the Polanyi–Semenov equation (Eq. (II)) for the homogeneous reactions of H-atom abstraction from hydrocarbons, from methane in particular,

$$X + CH_4 \rightarrow XH + CH_3, \tag{7}$$

where X is a gaseous species with an affinity to a hydrogen atom: atoms (H, O, F, Cl, Br, and I), radicals (OH, CH_3, CH_3O, CF_3, C_6H_5, and SH), and O_2 molecule.

Since it is believed that methyl radical formation is the rate determining step in the formation of ethane molecule, these data suggest the analogy between heterogeneous and homogeneous reactions of H-atom transfer from methane.

The second important parameter of oxide catalysts is oxygen binding energy $E_{[O]}$, that is, the energy required for O-atom abstraction from the oxidized surface active site [O]. Although the hydrocarbon activation step does not require catalyst oxygen abstraction, $E_{[O]}$ (together with with $E_{[O–H]}$) does control the mechanism and kinetics of the active site reoxidation [74] and, as a result, the rate of the steady-state reaction which proceeds via the Mars–van Krevelen redox mechanism. The value of $E_{[O]}$ also affects the rate of a heterogeneous–homogeneous reaction by controlling the activation energies of elementary reactions of the O-atom transfer.

The above idea receives further support from the results of the numerous spectroscopic structural studies (EPR, IR, and UV–Vis) and the reactivity of mechanochemically and chemically generated defects on the SiO$_2$ surface [75]. It has been demonstrated that (i) free methyl and ethyl radicals are formed when methane and ethane interact with certain surface species; (ii) the rates of such reactions are controlled by the thermochemistry of surface sites; and (iii) free radicals undergo heterogeneous transformations of three types proposed in [72,73]. The energy relationships are discussed

as governing factors for another type of heterogeneous–homogeneous reactions—surface-initiated pyrolysis [76].

The relationships between thermochemical and kinetic parameters made it possible to construct the kinetic scheme for the catalytic OCM process. This scheme accounts for several nontrivial effects in the OCM process:

— The complex effect of hydrogen peroxide;
— The existence and kinetic features of previously unknown mechanism of the catalyst reoxidation without intermediate dehydroxylation and formation of oxygen vacancies;
— The difference in the action of molecular oxygen and N_2O as oxidants.

Importantly, this scheme can be used an initial stage for developing the kinetic description of more realistic spatially distributed systems [77].

There are several factors hindering the progress in their kinetic description of ODH reactions, especially over the most efficient V and Mo-containing catalysts:

— The use of the above assumptions applicable to the OCM catalysts (as a rule, insulators which do not contain transition metal cations) is not well grounded in this case;
— Because of relatively high specific surface areas, the model should include a detailed description of the reactive diffusion of radical species inside the pores; although the examples of such description are known [78], it is not a well-developed area yet;
— The experimental measurements of the individual thermochemical parameters, $E_{[O-H]}$ and $E_{[O]}$, in the case of the ODH catalysts are much more difficult because of the rapid subsequent dehydroxylation, which follows the H-atom addition to the surface active site; this is presumably due to the lower $E_{[O-H]}$ and $E_{[O]}$ values compared to the OCM catalysts.

Nevertheless, there is an important consequence of thermochemistry–reactivity relationships. The extensive analysis of experimental data for numerous partial oxidation reactions has demonstrated [79] that their selectivity depends on the difference in the strengths of the weakest bonds in the reactant and the product molecules. This is evidently due to the differences in the activation energies of the initial steps for two substances. As mentioned above, the values of the parameters in Eq. (II) depend on the sign of ΔH, and the difference in E_a for two given hydrocarbons will be much greater for endothermic reactions compared to exothermic because $b_{exo} < b_{endo}$. Hence, for instance, in the pair "propane (reactant)–propylene (ODH product)" the difference in reactivity should be lower and ODH selectivity should be higher over a catalyst having active sites with higher $E_{[O-H]}$ provided both molecules are activated via the abstraction of H-atom from the weakest C–H bond. Using
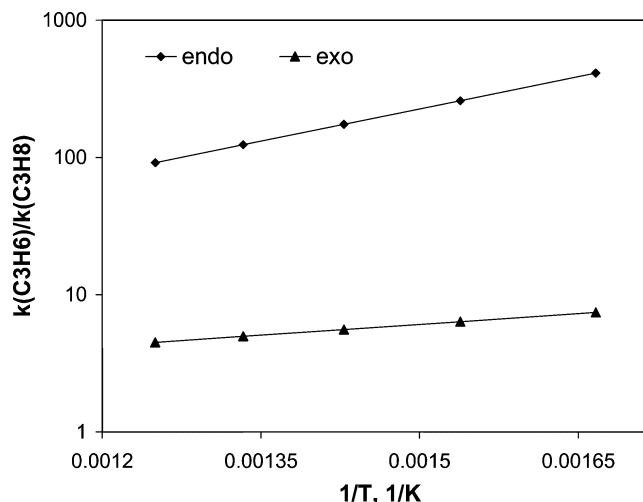

Fig. 3. Temperature dependence of the evaluated ratio of the rate constants for the reactions (1) with propylene and propane; the equal preexponentials are taken for two hydrocarbons.

the b values given above and taking into account that the difference in the dissociation energies of the weakest C–H bonds in C_3H_8 and C_3H_6 molecules is 40 kJ/mol [80], one can evaluate the ratio of the corresponding rate constants (assuming that the ratio of preexponential factors is close to 1). The results given in Fig. 3 show that at 800 K this ratio is ~ 90 and 4.5 for endothermic ($b = 0.75$) and exothermic ($b = 0.25$) reaction (1), respectively, and tends to decrease with an increase in temperature. This is a dramatic difference since it may cause the limiting ODH yield variation from ~ 1 to 14%.

The relative reactivities of propane and propylene evaluated above based on thermochemistry are within the same range as those obtained from kinetic measurements over Ni–Co molybdates [39], zirconia-supported V, Mo, and W oxides [45], and alumina-supported ODH catalysts [48]. Moreover, it was demonstrated that both hydrocarbons react over the same active sites, and the difference in the activation energy between propane ODH and propylene combustion (ΔE_a) decreases with an increase in the vanadia loading from 40 kJ/mol to nearly 0 over the V/Al$_2$O$_3$ catalysts. This decrease could be described in terms of the Polanyi–Semenov correlation, if the relevant thermochemical data for the catalysts used in these studies were available. In fact, for propane and propylene the ΔE_a value can vary in the same range: from 40 kJ/mol ("weak" active sites, positive ΔH) to 0 ("strong" active sites, highly negative ΔH). Unfortunately, for the reasons mentioned above the experimental measurement of $E_{[O-H]}$ is complicated. Available calorimetric experimental data [81] only indicate that the correlation between the oxygen binding energy $E_{[O]}$ and the ODH selectivity of V/Al$_2$O$_3$ catalysts does exist. However, this is insufficient for drawing any unambiguous conclusion.

Another interesting effect was observed when ethane and propane reactivities were compared over the same ODH catalyst [48]. It was found that in spite of the substantial

difference in the strengths of the weakest C–H bond in propane (in methylene group) and ethane (in methyl group) and much lower rates of reaction for ethane than for propane, there is no difference in the activation energies in their ODH. Although it is evident that this effect is due to kinetics and thermochemistry, no satisfactory explanation has been found yet.

5. Other oxidative transformations of light alkanes

It would be interesting to see whether or not the above concepts could be extended to any other catalytic oxidative reactions of light alkanes. In particular, some processes are widely believed to be strictly heterogeneous pathways, first of all those catalyzed by metals such as methane oxidation (total and partial) and steam reforming. In a series of publications by Bobrov et al. [82–85] it was shown that kinetic features of methane steam reforming over nickel and ruthenium catalysts are very similar to those observed in typical heterogeneous–homogeneous processes: the apparent rate constant of methane conversion and activation energy decrease at increasing catalyst loading or if the catalyst is diluted with carbonaceous material able to terminate free radical processes. Although these authors do not discuss any reaction scheme explaining the observed effects, they likely could be rationalized in the framework of the nonbranched chain reaction scheme proposed earlier by Lavrov and Petrenko [86]. They assumed that the process is initiated by homogeneous dissociation of methane
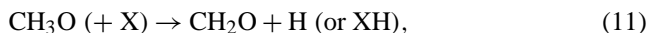
$$CH_4 \rightarrow H + CH_3 \tag{8}$$

and water molecule is activated on reduced metal sites Z as follows

$$Z + H_2O \rightarrow ZO + H_2. \tag{9}$$

The subsequent interaction of oxidized site ZO with gaseous radical species regenerates the catalyst

$$ZO + CH_3 \rightarrow Z + CH_3O. \tag{10}$$

The formation of carbon monoxide can occur via the sequence of homogeneous steps; for instance,

$$CH_3O (+ X) \rightarrow CH_2O + H \text{ (or XH)}, \tag{11}$$

$$CH_2O + X \rightarrow CHO + XH, \tag{12}$$

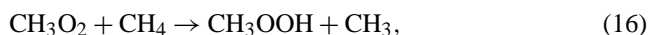$$CHO (+ X) \rightarrow CO + H \text{ (or XH)}. \tag{13}$$

In [82–85] it is also assumed that the methane molecule can undergo a dissociative adsorption followed by an escape of methyl radicals to the gas phase. The difference between two metals (Ni and Ru) is explained by a weaker binding of CH_3 radicals on ruthenium. The sequence of steps (8)–(13) can be added with chain propagation steps, such as

$$CH_4 + X \rightarrow CH_3 + XH. \tag{14}$$

If so, steps (8)–(14) and methane dissociation on metal surface compose a heterogeneous–homogeneous reaction network which qualitatively describes the phenomena observed in [82–85].

On examination of methane partial and total oxidation, let us restrict our consideration to the processes at short (millisecond) contact times. There are numerous examples of such processes, which proceed over woven materials, metal or metal-loaded monoliths (see, for instance [87]). Note that for each geometry of the reaction zone there is a certain threshold in linear gas velocities, above which the frequency of gas–solid collisions becomes less than the number of reactant molecules supplied onto the catalyst in a unit time. For instance, for a single-gauze catalyst this threshold is close to 1 m s^{-1}. With methane and oxygen sticking coefficients taken as 10^{-2} [88], we must conclude that a strictly heterogeneous reaction does not afford high degrees of conversion, which are observed experimentally. In other words, we should take into consideration a substantial contribution of gas phase reactions to the overall process. A reaction network in this case could include steps identical to (8)–(14) added with oxygen chemisorption on metal and chain-branching processes due to homogeneous reactions involving molecular oxygen; for instance,

$$CH_3 + O_2 \Leftrightarrow CH_3O_2, \tag{15}$$

$$CH_3O_2 + CH_4 \rightarrow CH_3OOH + CH_3, \tag{16}$$

$$CH_3OOH \rightarrow CH_3O + OH, \tag{17}$$

$$CH_3 + O_2 \rightarrow CH_3O + O. \tag{18}$$

Unfortunately, because of a substantial lack in kinetic data and a limited range of conditions under which the existing data have been collected one faces serious problems when trying to compose a detailed kinetic model even for traditional heterogeneous reaction pathways [88]. As to the heterogeneous reaction of free radical species, to date there are no well-grounded approaches to their description in the case of metal surfaces. An additional complication is caused by very large temperature and concentration gradients in reaction systems operated at short contact times [87]. Nevertheless, one may anticipate a substantial development in mechanistic studies of processes at short contact times and in their practical implementation in the near future.

6. Concluding remarks

The above analysis of light alkane catalytic oxidation indicates that:

- The formation of free alkyl radicals is the most energetically feasible process of the initial molecule activation;
- The observed kinetic regularities of the OCM and ODH reactions are characteristic of typical heterogeneous–homogeneous reactions;

– The overall reaction network includes both homogeneous and heterogeneous elementary reactions of primary and secondary free radicals;

– The heterogeneous reactions of free radicals can be described using the analogy with homogeneous reactions of the same types;

– Certain thermochemical parameters of surface active sites, particularly the H-atom affinity $E_{[O–H]}$ and the oxygen binding energy $E_{[O]}$ govern the kinetics of elementary heterogeneous reactions of free radicals and, to a large extent, the overall process kinetics;

– Further improvements in the methodology for the studies in this area are required to achieve a better understanding of heterogeneous reactions of free radicals and their role in catalytic processes.

In other words, although recent studies gave us an insight into the mechanism of light alkane oxidation, there is still a number of unsolved problems. Further success would require the use of advanced experimental techniques. In particular, the improvement of temporal resolution of calorimetric measurements and combining them with advanced transient response techniques (such as a TAP reactor [89]) are very promising since currently there are no other ways to obtain information on the thermochemical properties of nonequilibrium systems, such as working catalysts, under real reaction conditions.

On the other hand, the quantum chemical calculations of the structure of oxide systems and the interaction of hydrocarbon molecules with the active sites (see, for instance [90–97]) are becoming a powerful tool for elucidating the intrinsic mechanisms of catalytic reactions at the molecular scale. The use of quantum chemistry to obtain thermochemical information and kinetic parameters of elementary reactions [98] are of particular interest in view of the above discussion.

To conclude, it is worth noting that the high reactivity of heterogeneously generated free radicals can be utilized in designing the processes for converting light alkanes to valuable chemicals. As was shown recently [99,100], a nonadditive increase of acrolein yield from propane can be reached if the process is carried out in the combined catalyst layer, where propane activation and formation of free propyl radicals over one oxide catalyst is followed by their fast transfer to another capable of converting them into acrolein. The possibility of such synergy was predicted by Grasselli shortly before that study [101]. Another example of this kind was recently found in the system containing an active OCM catalyst (Nd/MgO) and relatively inert metal filament (Ni-based alloy) [58,102,103]: the addition of the metal leads to a shift in product distribution (from C_2 hydrocarbons to CO and H_2), to a sharp increase in the overall rate of reaction, and to a complex dynamic (oscillatory) behavior. Note that in the processes of this type the implication of macrokinetic factors, mass transfer in particular, can play a key role. Since in a combined catalytic system free radicals generated on the surface of one solid can further react on the same surface, on the surface of the second catalyst, as well as in the gas phase, the apparent kinetic behavior is an interplay of chemical and mass transfer processes. On the one hand, this makes the system very complex to control. However, on the other hand, the high reactivity of free radicals easily formed from relatively inert alkanes can lead to previously unexpected achievements in the development of new-generation catalytic processes.

Acknowledgments

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