ELSEVIER

Catalysis Today 61 (2000) 287–293

CATALYSIS TODAY

www.elsevier.com/locate/cattod

On the role of heterogeneous and homogeneous processes in oxidative dehydrogenation of C_3-C_4 alkanes

V.P. Vislovskiy [a,1], T.E. Suleimanov [a], M.Yu. Sinev [b,2],
Yu.P. Tulenin [b], L.Ya. Margolis [b], V. Cortés Corberán [c,*]

[a] *Institute of Inorganic and Physical Chemistry, Azerbaijan Academy of Sciences, 29 H. Javid ave., 370143 Baku, Azerbaijan*
[b] *Semenov Institute of Chemical Physics, RAS, 4 Kosygin str., Moscow 117334, Russia*
[c] *Instituto de Catálisis y Petroleoquímica, CSIC, Campus UAM Cantoblanco, 28049 Madrid, Spain*

Abstract

The effects of reactor arrangement, catalyst particle size and void volume on the oxidative dehydrogenation (ODH) of propane and *iso*-butane are studied. In an empty quartz reactor, a high conversion of alkane (up to 36% with a 40% ODH selectivity) can be achieved. Packing of the reactor with different solids (quartz, γ-Al_2O_3, complex V-containing oxide catalysts) leads to a drastic change in reaction parameters, which is strongly dependent on the chemical nature of solids and their particle size. The analysis of observed phenomena indicates that: (a) the termination of gas-phase chain reaction takes place on the surface of any solid material; (b) certain solids behave as active generators of free radicals, thus initiating the new reaction pathway which develops both in the gas-phase and on the solid surface. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Heterogeneous and homogeneous processes; Oxidative dehydrogenation; C_3-C_4-alkanes; Vanadium-antimony oxide catalysts

1. Introduction

Due to the low reactivity of paraffin molecules, their catalytic oxidative dehydrogenation (ODH) proceeds at elevated temperatures at which homogeneous gas-phase processes may take place. The contribution of homogeneous factors in heterogeneous catalytic reactions has been discussed repeatedly (see, for instance, [1–4]). However, for each particular process, additional experimental data and kinetic analysis are required in order to elucidate if homogeneous steps are just side reactions or they take part in the main route and play an important role in the formation of the desired products.

As it was demonstrated in [4], in many cases the analysis of kinetic features of the process makes it possible to elucidate the role of homogeneous factors in heterogeneous catalytic reactions and to reveal the contribution of each (i.e. homogeneous and homogeneous) component in the overall process. Among others, the method of variation of the void reactor volume has been successfully utilized for this purpose [1,2,4]. More specifically, Nguyen and Kung [5] used the expedient of the gas flow reverse when a void space is present in the reactor on just one side of the catalyst layer. Non-additive character of propane ODH over the thin layer of V-Mg oxide catalyst and in the void

---

[*] Corresponding author. Fax: +34-91-585-4760.
E-mail addresses: vislovski@mail.ru (V.P. Vislovskiy), sinev@center.chph.ras.ru (M.Yu. Sinev), vcortes@icp.csic.es (V. Cortés Corberán).
[1] Fax: +994-12-977-456.
[2] Fax: +7-095-938-2156.

0920-5861/00/$ – see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S0920-5861(00)00386-2

gas volume was demonstrated, and the observed product distribution was explained by the chain reaction in the gas-phase.

It was shown in [6] that the size factor, i.e. the characteristic size of the free gas space, may have a substantial effect on the features of the overall reaction when it has a complex heterogeneous–homogeneous nature.

In this study, the combination of these approaches was used to reveal the role of homogeneous and heterogeneous factors in ODH of propane and *iso*-butane, particularly in the presence of supported V-Sb oxide-based multicomponent catalysts. These catalysts were shown to be highly efficient in the ODH of lower alkanes at elevated temperatures, but the mode of their action has not been well understood yet.

2. Experimental

2.1. Catalysts

Two series of V-Sb oxide-based catalysts were prepared by impregnation of γ-alumina with mixed aqueous solutions containing the appropriate amounts of NH_4VO_3, $SbCl_3$, $SnCl_2$ and metal nitrates. For the large grain catalysts (series “L”), microspheric γ-alumina (BET specific surface area $85\,m^2\,g^{-1}$, particle size 1.8–2.0 mm) was taken. To prepare the small grain catalysts (series “S”), the same γ-alumina was crushed and sieved and particles of 0.3–0.8 mm size were used. After impregnation, all samples were dried at 100–120°C and calcined at 650°C in the same way. The amounts of vanadium and antimony in all catalysts were the same (17.73 wt.% calculated on the basis of $VSb_{1.25}O_{4.4}$); other elements were taken as minor additives.

2.2. Setup

ODH of propane and *iso*-butane was carried out at atmospheric pressure. Two different types of quartz reactors were used. The U-shape reactor is presented in Fig. 1. In this reactor catalyst was placed into the central part of elbow A; void volume of the reactor had a constant quartz chips filling (particle size 0.5–1.0 mm), except the space above the catalyst layer. In this space, the height of void zone filled with quartz chips (h) was varied from 5 to 135 mm. The direction of the gas flow was also varied by switching inlet/outlet from elbow A to B. In this way, the variable quartz filled zone was located either upstream or downstream the catalyst layer.

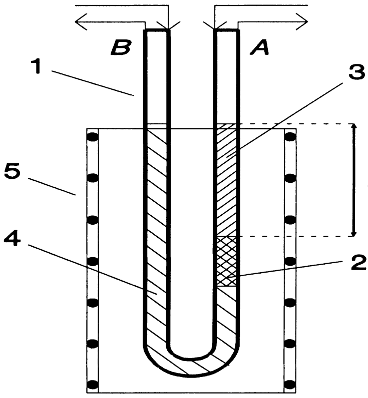

Fig. 1. U-shape reactor design — 1: quartz reactor, 2: catalyst layer, 3: varying quartz filling, 4: constant quartz filling, and 5: electric furnace; A and B are the gas inlet/outlet elbows; *h* the varying filling height.

For comparison, a straight reactor, having a very narrow hot zone, was used in the experiments in which the contribution of gas-phase processes before and after the catalyst layer was reduced to a minimum.

An on-line GC analysis of the reaction mixture was carried out using two columns packed with Porapak-Q (CO_2, C_2–C_4 hydrocarbons) and molecular sieve NaX (H_2, N_2, O_2, methane, CO) and TC-detectors.

3. Results

The results obtained in *iso*-butane oxidation over selected catalysts in the U-shape reactor are presented in Table 1. In the empty reactor, a high conversion of *iso*-butane ($X\approx36\%$) can be reached at 550°C, with relatively low ODH selectivity ($S_{ODH}\approx40\%$). Placing different solids into the reactor leads to a drastic change in reaction parameters, which are strongly dependent on the chemical nature of solids and on the filling of the reactor interior: in the same conditions, i-C_4H_{10} conversions vary from ~1% if the reactor is filled with quartz chips to ~35% in the presence of complex V-Sb oxide catalysts with S_{ODH} exceeding

Table 1
ODH of *iso*-butane in the U-shape reactor (550°C, 22% $i\text{-}C_4H_{10}$+12% O_2 in N_2, total flow 54.5 ml/min, V_{cat}=4 ml)

Catalyst[a]	Inlet	*h* (mm)	Conversion of $i\text{-}C_4H_{10}$ (%)	Selectivities (%)				Yield of $i\text{-}C_4H_8$ (%)
				$i\text{-}C_4H_8$	C_1–C_3	CO_2	CO	
Unpacked reactor	A	0	35.9	40.0	51.2	2.9	5.9	14.4
Quartz chips	A	135	1.3	58.8	31.1	10.0	Trace	0.7
γ-Alumina, S	A	135	8.2	29.1	4.1	39.3	27.5	2.4
γ-Alumina, L			14.4	26.7	10.8	34.4	28.1	3.8
VSbCr/Al_2O_3, S	A	135	12.5	74.0	11.6	7.1	7.3	9.3
VSbCr/Al_2O_3, L			18.9	75.6	4.9	12.9	6.6	14.3
VSbCr/Al_2O_3, L	A	0	34.5	59.5	21.0	14.0	5.5	20.5
VSbSn/Al_2O_3, S	A	135	4.2	77.4	5.6	13.6	3.4	3.2
VSbSn/Al_2O_3, L			21.0	67.6	7.2	15.8	9.4	14.2
VSbNi/Al_2O_3, S	A	135	12.8	77.3	8.7	9.6	4.4	9.9
VSbNi/Al_2O_3, L			17.0	68.7	8.0	13.4	9.9	11.7
VSbCrNi/Al_2O_3, S	A	135	10.0	71.9	11.8	9.4	6.9	7.2
VSbCrNi/Al_2O_3, L			19.2	68.8	8.6	15.2	7.4	13.2
VSbBiBa/Al_2O_3, S	A	135	26.6	71.3	10.3	9.8	8.6	19.0
VSbBiBa/Al_2O_3, L			30.2	72.2	7.3	14.4	6.1	21.8
VSbBiBa/Al_2O_3, S	B	5	11.6	76.1	12.8	6.8	4.3	8.8
	B	55	11.8	77.6	10.9	6.6	4.9	9.2
	B	135	13.6	74.0	15.6	6.1	4.3	10.1
VSbBiBa/Al_2O_3, L	B	5	33.3	65.9	16.1	7.9	9.1	21.9
	B	35	25.8	70.6	11.0	14.1	4.3	18.2
	B	55	23.5	72.6	7.2	15.0	5.2	17.1
	B	135	16.3	70.7	12.1	12.5	4.7	11.5

[a] S: series "S", L: series "L".

75%. Besides, a strong effect of catalyst-free space downstream and upstream of the catalyst layer was observed when packing of void volume and direction of gas flow were varied.

The overall reaction parameters are strongly affected by catalyst particle size. Although the results obtained over different catalysts vary in a wide range, as a whole the values of alkane conversions substantially increase from "S" to "L" series catalysts of the same composition without any significant decrease in S_{ODH}. Among V-containing samples this difference in conversions increases at decreasing efficiency of series "S" catalysts. If catalysts of series "L" are crushed and sieved, their catalytic performance becomes the same as that observed for corresponding series "S" samples indicating that this phenomenon should be attributed to the influence of particle size on the process itself, but not on the procedure of catalyst preparation.

It is important to notice that the effects of void volume and of particle size are interconnected: gradual filling of the post-catalytic void volume has much stronger effect in the case of series "L" catalyst (see Fig. 2). Results obtained over the catalysts of different particle sizes become closer as the height of the post-catalytic zone filled with quartz increases.

In the case of straight-shape reactor, packing with quartz suppresses also the non-catalytic alkane oxidation. In the case of propane, total conversion at 550°C is 0.6%, rising to 1.8% at 650°C; *iso*-butane conversions at 550 and 600°C are ∼1 and ∼3%, respectively. Propane is less reactive compared to *iso*-butane in catalytic oxidation too (see Fig. 3). Over the whole series of vanadium-containing catalysts S_{ODH} increases at rising temperature with an exception of experiments in which alkane conversion exceeds ∼40%. The latter

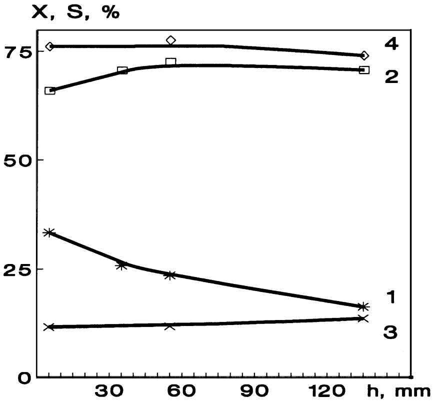

Fig. 2. i-C_4H_{10} conversion (1, 3) and S_{ODH} (2, 4) as functions of post-catalyst quartz-packed zone height; 550°C, 22% i-C_4H_{10}+12% O_2 in N_2; (1, 2) VSbBiBa/Al_2O_3, L; (3, 4) VSbBiBa/Al_2O_3, S.

rule is general, no matter which reactor (U-shape or straight) is used.

Another factor strongly affecting the ODH selectivity is oxygen concentration. In the whole temperature range studied here S_{ODH} gradually decreases at increasing oxygen content in the initial mixture (see Fig. 4). Simultaneously the alkane conversion increases leading to the appearance of a flat maximum in the olefin yield at initial oxygen concentrations around 7–10 vol.%.

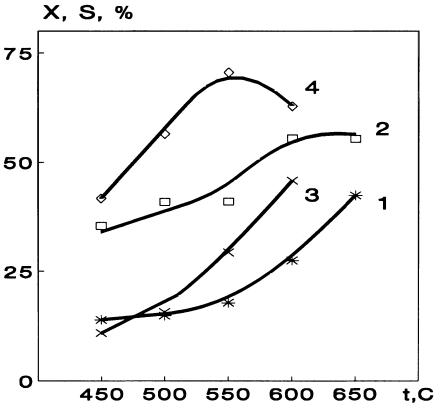

Fig. 3. Propane (C_3) and iso-butane (i-C_4) conversions (X) and S_{ODH} as functions of temperature over VSbBiBa/Al_2O_3, L; 22% alkane+12% O_2 in N_2; 1: $X(C_3)$, 2: $S(C_3)$, 3: $X(i\text{-}C_4)$, 4: $S(i\text{-}C_4)$.

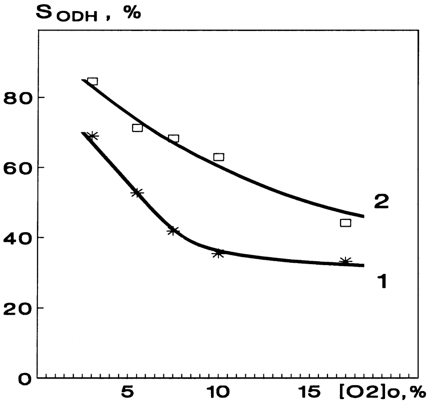

Fig. 4. iso-Butene selectivity as a function of oxygen concentration in the initial mixture; $[i\text{-}C_4H_{10}]_0$=15 vol.%; (1) 335°C, (2) 550°C.

4. Discussion

4.1. Non-catalytic oxidation and effect of reactor packing

The results obtained in the unpacked reactor show that in the conditions which are optimal for catalytic ODH, homogeneous oxidation of C_N alkanes (N=3 and 4) proceeds with high rate. The main route of this chain reaction leads to the formation of corresponding olefins and cracking products (C_1–C_{N-1} hydrocarbons), likely due to the rapid decomposition of alkyl radicals formed in the initiation step. For instance, in the case of iso-butane some of these steps are

$$(CH_3)_3CH + O_2 \rightarrow (CH_3)_3C^\bullet + HO_2^\bullet \qquad (1)$$

$$(CH_3)_3C^\bullet \rightarrow CH_2{=}C(CH_3)_2 + H^\bullet \qquad (2)$$

$$(CH_3)_3C^\bullet + O_2 \rightarrow CH_2{=}C(CH_3)_2 + HO_2^\bullet \qquad (3)$$

$$\begin{aligned}(CH_3)_3C^\bullet + O_2 &\Leftrightarrow (CH_3)_3 + CO_2^\bullet\\ &\rightarrow CH_2{=}C(CH_3)_2 + HO_2^\bullet \qquad (4)\end{aligned}$$

$$(CH_3)_3C^\bullet \rightarrow CH_2{=}CHCH_3 + CH_3^\bullet \qquad (5)$$

$$(CH_3)_3CH + CH_3^\bullet \rightarrow (CH_3)_3C^\bullet + CH_4 \qquad (6)$$

$$(CH_3)_3C^\bullet \rightarrow CH_2{=}CH_2 + C_2H_5^\bullet \qquad (7)$$

$$(CH_3)_3CH + C_2H_5^\bullet \rightarrow (CH_3)_3C^\bullet + C_2H_6 \qquad (8)$$

The final hydrocarbon product distributions are controlled by competing steps of primary alkyl radical transformations. As the data given in Table 1 show, in the case of unpacked reactor cracking processes (5)–(8) dominate over dehydrogenation steps (2)–(4). Besides, the amount of CO in this case is substantially higher than that of CO_2. This is also characteristic for homogeneous oxidation which proceeds via peroxy-type radicals.

If the reactor is packed with any solid material, the features of the process change drastically. The product distributions obtained in experiments with any packing show the shift from cracking hydrocarbon products to dehydrogenation and oxidation, and CO_2 becomes the predominant carbon oxide. Similar regularities were mentioned in propane oxidation by Nguyen and Kung [5]. It is important to notice that these changes are independent of the chemical nature of the packing material, its particle size, catalytic activity and ODH selectivity. Moreover, such a strong effect of packing cannot be explained by some decrease (2–5 times depending on the particle size distribution) in residence time. This indicates that any oxide surface not only terminates free radical processes, but also modifies them in some similar way.

4.2. Effect of catalyst particle size

It is evident that the kinetic features of reaction which proceed on the surface of a catalyst may depend on its particle size only if some diffusional restrictions take place. In this case, the larger the particles, the more pronounced the restrictions. In other words, the measured rate of reaction should decrease at increasing catalyst particle size. As a rule, selectivity with respect to any partial oxidation products also tends to decrease due to consecutive total oxidation processes inside catalyst pores.

The results presented in Table 1 demonstrate a reverse behavior of the process under study. From all the studied catalysts, including undoped γ-alumina, we infer that the larger the particle size, the higher the alkane conversion. In some cases up to fivefold increase of conversion is reached.

It can be easily demonstrated that in the layer formed by closely packed spheres of uniform size the volume of free space is independent of diameter of spheres. In the case of catalysts under study, the difference between series “S” and series “L” catalysts consists in

1. characteristic size of gaps between particles in the packing of the layer, and
2. free volume of gas-phase (“secondary porosity”) inside the catalyst layer due to a wider particle size distribution in series “S” samples.

Because of these two factors, gas-phase reactions have more chance to develop inside the catalyst layer in the case of series “L” catalysts. According to the analysis performed in [6], if the reaction proceeds via the formation and transformations of free radicals which undergo simultaneously heterogeneous and gas-phase processes, the contribution of the gas-phase in the overall rate of reaction (and conversion of reactants) increases drastically when the characteristic sizes of gas gaps increase from 10^{-2} to 1 mm. This is exactly the scale of sizes which is covered by the switch from series “S” to series “L” samples.

It is important to notice that in the case of series “L” samples we did not observe any drastic fall in ODH selectivity which one could expect upon increasing alkane conversion or any other serious shifts in product distributions towards those characteristic for homogeneous alkane oxidation. Therefore, one may conclude that although the total conversion increases with catalyst particle size due to the increasing contribution of gas-phase processes, the product distributions remain controlled by the properties of catalyst, i.e. homogeneous and heterogeneous steps are strongly interconnected.

4.3. Effect of reactor post- and pre-catalytic void volume

As we mentioned above, the reverse flow method was used in [5] to study the contribution of the void volume in the catalytic ODH of propane. It was shown that additional conversion of propane in the pre-catalytic void volume takes place due to the influence of heat generated by working catalyst wafer. In the case of our experiments over the layer of granular catalyst separated from the void volume by more or less thick quartz packing, no effect of the pre-catalytic void volume was observed. Moreover, when series “S” catalyst was used, no pronounced effect of the post-catalytic volume was also observed (see Table 1). This means that we may neglect any thermal effects for the analysis of obtained results.

If the series “L” VSbBiBa/Al_2O_3 catalyst is used, the alkane conversion nearly doubles when the variable quartz packing height decreases from 135 to 5 mm. If one assumes that this effect is due to the homogeneous oxidation taking place in the post-catalytic void volume, it is possible to calculate the parameters of the reaction downstream of the catalyst layer by subtracting the amounts of products formed in the experiment with h=135 mm from those formed in the experiments with lower packing. Let us symbolize the conversions, selectivities and yields of product i obtained at packing height h as $X(h)$, $S_i(h)$ and $Y_i(h)$, respectively, and corresponding parameters obtained at h=135 mm as $X(135)$, $S_i(135)$ and $Y_i(135)$. The additional conversions ΔX and corresponding selectivities $S(\Delta)_i$ attributed to product i formation in the post-catalytic volume can be calculated from the Table 1 data as follows:

$$\Delta X = X(h) - X(135)$$

$$S(\Delta)_i = \frac{\Delta Y_i}{\Delta X} = \frac{X(h)S_i(h) - X(135)S_i(135)}{X(h) - X(135)}$$

where $\Delta Y_i = Y_i(h) - Y_i(135)$.

The comparison of the calculated values of ΔX and $S(\Delta)_i$ given in Table 2 with the data of Table 1 indicate that the product distributions (especially cracking to dehydrogenation ratios) in the post-catalytic void volume and in the unpacked reactor differ significantly. The lesser the unpacked void volume, the more the difference. In other words, the processes inside the catalyst layer and in the post-catalytic volume are non-additive, and the gas-phase downstream of the catalyst “feels” somehow the presence of the catalyst and its properties. The absence of pronounced effects at h variations in our experiments with series “S” catalyst gives another corroboration of this statement. As for now, the nature of this “feedback control” is an open question. One of the possible explanations is a diffusional counterflow of radicals from the void volume to the catalyst layer.

4.4. Heterogeneous–homogeneous reaction network

First, let us summarize the conclusions which can be derived from our experimental data:

1. Homogeneous and catalytic oxidation of propane and *iso*-butane proceed in the same range of temperatures.
2. Packing of the reactor with any solid sharply decreases the rate of homogeneous oxidation and modifies the product distributions.
3. Even in the presence of active catalyst, alkane oxidation can proceed in the free gas gaps between catalyst particles and in the post-catalytic void volume.
4. Homogeneous processes accompanying the reaction over the catalyst are very sensitive to the density of packing and/or to the linear dimensions of gas gaps inside the catalyst layer and in the post-catalytic void volume.

These experimental results strongly suggest that parameters of the overall process are dependent on the combination of heterogeneous and homogeneous factors. This combination may be presented in general terms as follows. Reaction starts from the homolytic C–H bond cleavage assisted by the surface oxidizing center [O] with free radical formation analogous to the gas-phase initiation reaction (1):

$$[O] + (CH_3)_3CH \rightarrow [OH] + (CH_3)_3C^{\bullet} \qquad (9)$$

Over active V-Sb oxide catalysts the rate of step (9) is likely to exceed significantly the rate of homogeneous initiation reaction (1). Further development of the process depends on the fate of the initial free alkyl radical formed. Of course, they can undergo all

Table 2
Parameters of *iso*-butane oxidation over series “L” VSbBiBa/Al_2O_3 catalyst at varied quartz packing height (calculated from the Table 1 data)

h (mm)	ΔX (%)	$S(\Delta)_{ODH}$ (%)	$S(\Delta)_{crack.}$ (%)	$S(\Delta)_{CO_2}$ (%)	$S(\Delta)_{CO}$ (%)	Crack./ODH	CO/CO_2
5	17	61.3	19.9	3.5	13.3	0.325	3.82
35	9.5	70.4	9.1	16.85	3.6	0.13	0.21
55	7.2	76.9	−3.9	20.65	6.3	−0.051	0.31
135	0	–	–	–	–	–	–

kinds of transformations which take place in the homogeneous chain reaction, including reactions (2)–(8). Moreover, as the data obtained with series “L” catalysts indicate, chain reaction can develop even in the gas gaps between catalyst particles. However, as the product distributions indicate, in the presence of a catalyst alkyl radicals rapidly react with another [O] site forming an olefin molecule:

$$[\mathrm{O}] + (\mathrm{CH_3})_3\mathrm{C}^\bullet \rightarrow [\mathrm{OH}] + \mathrm{CH_2{=}C(CH_3)_2} \qquad (10)$$

As a result, the rate of dehydrogenation exceeds by far the rate of cracking processes and ODH selectivity sharply increases.

The observed trends in S_{ODH} at varied temperature and oxygen concentration could be understood as follows. The activation energy of step (10) is likely to be very low, and one has to assume that the observed increasing ODH selectivity indicates the decreasing contribution of some oxidation process at increasing temperature. As we mentioned above, gas-phase total oxidation proceeds via peroxy radicals. Any of them can easily react with other radical species in the gas, for instance, with alkyl radicals forming alkoxy species:

$$(\mathrm{CH_3})_3\mathrm{C}^\bullet + \mathrm{RO_2}^\bullet \rightarrow (\mathrm{CH_3})_3\mathrm{CO}^\bullet + \mathrm{RO}^\bullet \qquad (11)$$

and oxidize olefin molecules to corresponding olefin oxides. In the ODH conditions, both alkoxy radicals and olefin oxides undergo a series of rapid consecutive transformations leading to CO formation. These transformations, as a rule, proceed with low activation energies and their contribution to the overall process at low temperatures is relatively high. Moreover, at low temperatures the equilibrium in the reaction (4) is shifted to the right increasing the relative amount of peroxy radicals and causing the fall of S_{ODH}. On the other hand, the increasing oxygen concentration also enhances the $\mathrm{RO_2}^\bullet$ formation via reactions (3) and (4).

When catalysts are present in the reactor, the decreasing $\mathrm{CO/CO_2}$ ratio indicates that in this case mainly heterogeneous total oxidation takes place. The latter can proceed via the capture of free radicals by the surface active site:

$$[\mathrm{O}] + (\mathrm{CH_3})_3\mathrm{C}^\bullet \rightarrow [\mathrm{OC(CH_3)_3}] \qquad (12)$$

and consecutive attack of surface alkoxy intermediates by lattice and/or gaseous (adsorbed) active oxygen species leading to the formation of $\mathrm{CO_2}$ via surface carboxylate and carbonate intermediates. This process is very likely to compete with β-elimination of olefin:

$$[\mathrm{OC(CH_3)_3}] \rightarrow [\mathrm{OH}] + \mathrm{CH_2{=}C(CH_3)_2} \qquad (13)$$

Such a competition can also contribute to the selectivity trends at increasing temperature.

The final reaction network consisting of a number of heterogeneous and gas-phase homogeneous steps of formation and transformations of free radicals should be analyzed in terms of heterogeneous chemistry of free radicals. Evidently, the composition of gas mixture, first of all the absolute and relative concentrations of different radical species, in the presence of catalyst differ from that existing in a homogeneous reaction to an extent that final product distributions are different. In any event, this subject requires an additional analysis.

Acknowledgements

This study has been carried out under the financial support of the EC INCO COPERNICUS Programme (Project # IC15-CT96-0725 “CALIPSO”) and the Russian Foundation for Basic Research (RFBR Grant # 98-03-32183) which the authors greatly appreciate. We also acknowledge a helpful contribution of Dr. Viktor Sheinin.

References

[1] Ya.B. Gorokhovatskii, T.P. Kornienko, V.V. Shalya, Heterogeneous–Homogeneous Reactions, Tekhnika, Kiev, 1972.
[2] L.Ya. Margolis, Oxidation of Hydrocarbons over Heterogeneous Catalysts, Khimiya, Moscow, 1977.
[3] D.J. Driscoll, K.D. Campbell, J.H. Lunsford, Adv. Catal. 35 (1987) 139.
[4] M.Yu. Sinev, L.Ya. Margolis, V.N. Korchak, Uspekhi Khimii (Russ. Chem. Rev.) 64 (1995) 373.
[5] K.T. Nguyen, H.H. Kung, J. Catal. 122 (1990) 415.
[6] M.Yu. Sinev, L.Ya. Margolis, V.Yu. Bychkov, V.N. Korchak, Stud. Surf. Sci. Catal. 110 (1997) 327.