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Hydrogen formation during dehydrogenation of C_2–C_4 alkanes in the presence of oxygen: oxidative or non-oxidative?

Mikhail Yu. Sinev[a,*], Zukhra T. Fattakhova[a], Yurii P. Tulenin[a],
Pavel S. Stennikov[a], Vladislav P. Vislovskii[b]

[a] N.N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin street, Moscow 119991, Russia
[b] Institute of Inorganic and Physical Chemistry, Baku, Azerbaijan

Abstract

The main advantage of oxidative dehydrogenation (ODH) of light alkanes over non-oxidative dehydrogenation (NODH) is the absence of thermodynamic limitations for olefin per-pass yield. It is shown, however, that considerable amounts of molecular hydrogen are formed (in some cases—equivalent to the amounts of produced olefin or even higher) over typical ODH oxide catalysts when C_2–C_4 alkanes and oxygen are present in the feed gas. The analysis of product yields as functions of reaction parameters (temperature, flow rate, hydrocarbon-to-oxygen ratio) over a series of V- and Sb-containing ODH catalysts has shown that the main kinetic features cannot be described in the framework of a single mechanism. NODH, coking and free-radical oxidation are considered as the most important H_2 formation pathways. The ways to optimize the olefin production depending on the predominant mechanism of hydrogen formation over a particular catalyst are discussed.

Keywords: Oxidative hydrogenation; Non-oxidative dehydrogenation; C_2–C_4 alkanes

1. Introduction

Oxidative dehydrogenation (ODH) of light alkanes attracts a considerable attention as a potentially efficient way to produce olefins from relatively cheap and abundant feedstocks (see, for instance [1–5]). The main usually discussed advantage of ODH over non-oxidative dehydrogenation (NODH) of the same alkanes is the absence of thermodynamic limitations for per-pass olefin production since in the case of NODH an upper limit of yield determined by equilibrium (Y_{eq}) cannot be exceeded. As a first approximation, the following expressions determining equilibrium formation of olefin can be used:

$$[\text{olefin}]_{eq} = K_{eq}[\text{alkane}]_{eq}[H_2]_{eq} \tag{1}$$

or

$$Y_{eq}^2(1 - Y_{eq})^{-1} = K_{eq}P_0^{-1} \tag{2}$$

and

$$K_{eq} = \exp\left(-\frac{\Delta H}{RT} + \frac{\Delta S}{R}\right) \tag{3}$$

where $[\text{olefin}]_{eq}$, $[\text{alkane}]_{eq}$, $[H_2]_{eq}$ are the equilibrium concentrations of olefin, initial alkane and hydrogen, respectively; K_{eq} is the equilibrium constant; P_0 the total pressure ($P_{alkane} + P_{olefin} + P_{H_2}$); T the temperature; ΔH and ΔS the enthalpy and entropy changes in the following NODH reaction:

$$C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2 \tag{1'}$$

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[*] Corresponding author. Tel.: +7-95-939-7547; fax: +7-95-938-2156.
E-mail address: sinev@center.chph.ras.ru (M.Yu. Sinev).

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Based on the detailed thermodynamic data given in [6], the temperatures for moderate 50% olefin yields from ethane, propane and butanes were evaluated in [4] as 725, 595 and 540 °C, respectively. In principle, the removal of hydrogen from the reaction system by any means helps to eliminate the thermodynamic limitations for olefin formation. For instance, selective in situ burning of hydrogen formed over NODH catalyst enables to increase olefin yields [2,7,8]. However, catalytic ODH is considered as the most promising way to avoid thermodynamic limitations and necessity of external heating during the production of olefins from light alkanes. Indeed, if oxidant (e.g. molecular oxygen) is added to the feed gas the process becomes thermodynamically favorable at any level of alkane conversion and olefin yield. The only condition which has to be provided is water formation instead of H_2.

In real practice, however, neither water, nor hydrogen are usually measured experimentally when the reaction mixture is analyzed by on-line gas chromatography (GC). An accurate analysis of water requires additional complications of sampling system. As to the GC analysis of molecular hydrogen, some problems are discussed below. As a result, the analysis of experimental sections of publications dealing with ODH of light alkanes shows that in most cases in these studies only carbon balance is a subject of concern and the fate of hydrogen abstracted from alkane molecule cannot be traced because neither H_2, nor water are analyzed.

On the other hand, it is well known that substantial amount of hydrogen are formed during the oxidative coupling of methane (OCM) (see, for instance [9]) which is relative to ODH process (both reactions require elevated temperatures; they both proceed via the abstraction of H-atom from C–H bond; OCM catalysts are very efficient in ODH). The detailed studies of hydrogen formation during oxidation of C_2–C_4 alkanes over a series of typical ODH catalysts undertaken in this work indicates that the reaction pathways are much more complicated than it has been believed previously.

2. Experimental

In this study, a series of typical ODH catalysts, mainly belonging to the family of V- and Sb-based complex oxides supported on alumina, are studied. The details of preparation and characterization of these systems are described elsewhere [10–12]. In particular, in this study we used supported V- and Sb-containing catalysts prepared by impregnation of microspherical γ-Al_2O_3 (produced by MNTK Katalizator, Novosibirsk, Russia, specific surface area 85 m^2/g, particle size 0.3–0.8 mm) with water solutions containing appropriate amounts of ammonium vanadate, antimony trichloride and metal nitrates, drying and final calcination at 600 °C. V, Sb, Bi and Ba content in catalysts was 5.8, 11.9, 5.5 and 0.1 wt.%, respectively.

Oxidation of C_2–C_4 alkanes (ethane, propane and *iso*-butane) in a continuos-flow regime was studied in a fixed-bed quartz reactor equipped with a thermocouple placed inside the catalyst bed and operated at atmospheric pressure. Experiments were carried out at varied temperatures, flow rates, catalyst loading and alkane-to-oxygen ratios. Oxidative treatments of catalysts (pre-oxidation and reoxidation) were carried out in the same reactor by air flow at 600 °C. As we demonstrated earlier [10], in the similar reactor packed with quartz chips, the degree of *iso*-butane conversion does not exceed 1.3% at 550 °C. One may expect that conversions of less reactive C_2–C_3 paraffins should be even lower in the same conditions.

Analysis of reaction mixture was performed by on-line GC using chromatographs ("Chrom 5") with thermal conductivity detectors (TCD). The following stainless-steel columns (3 m length/3.5 mm inner diameter) were used for the separation of reaction mixture:

- packed with NaX molecular sieves working at 40 °C—to separate H_2, O_2, N_2, CH_4 and CO;
- packed with Porapak Q working at 50 °C—to separate CO_2, C_2H_4, C_2H_6;
- packed with GC Durapak working at 50 °C—to separate C_3–C_4 hydrocarbons.

GC analysis of hydrogen requires a special consideration. Molecular hydrogen can be easily separated from other permanent gases (O_2, N_2, CH_4 and CO) using columns packed with molecular sieves. However, the most widely used combinations of carrier gases and detectors have their specific drawbacks from the viewpoint of hydrogen detection. First, flame ionization detectors (FID), which are very sensitive to hydrocarbons and other organic molecules with high content of non-oxidized carbon atoms, cannot detect H_2

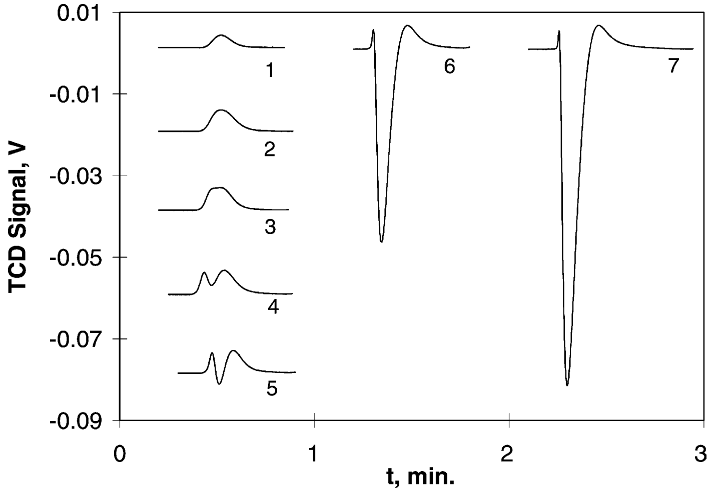

Fig. 1. Variations of H_2-peak shape with concentration of H_2 in the analyzed gas mixture. GC column: NaX molecular sieves (3 m × 3.5 mm); column temperature: 40 °C; He flow: 30 ml/min; loop volume: 1.65 ml; TCD current: 100 mA (1, 5%; 2, 10%; 3, 15%; 4, 25%; 5, 30%; 6, 67%; 7, 100%).

molecules in principle. When a GC system is equipped with a TCD, helium is normally used as a carrier gas (instead of other relatively cheap and accessible inert gases, such as argon or nitrogen) in order to increase the sensitivity to the main components of the reaction mixture, first of all to hydrocarbons, carbon oxides and oxygen. In contrast with those gases, hydrogen has much smaller and reverse difference in thermal conductivity with respect to helium. As a result, in typical GC system arrangements and conditions it is not possible to obtain "normal" calibration curves at varied concentrations of hydrogen in the analyzed gas.

A typical example of complex behavior of hydrogen peak in certain conditions of GC analysis is presented in Figs. 1 and 2. In this case, helium was used as a carrier gas, gas probes were injected into the helium flow using a six-port sampling valve with

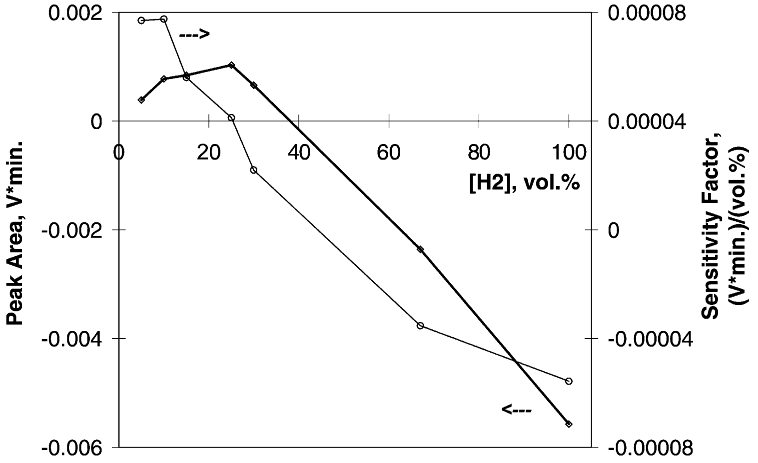

Fig. 2. H_2-peak areas and sensitivity factors as function of H_2 in the analyzed gas mixture (for conditions, see Fig. 1).

a 1.6 ml loop and after passing through the above described column with NaX molecular sieves the flow reached the TCD. As can be seen from Fig. 1, at hydrogen concentrations below 15% a "normal" shape of the peak is observed. However, the sign of the signal in this case is opposite to that which could be predicted based on the ratio of thermal conductivities of He and H_2. At increasing concentration, a "negative" component in the TCD signal appears and increases making the shape of the peak complex. When hydrogen concentration exceeds ~25 vol.%, this "negative" component crosses the baseline, and after 40 vol.% the net peak area becomes negative. These features do not change qualitatively at any variations of molecular sieve type, column size and temperature, helium flow rate and sampling loop volume. Although in principle the combination of peak shapes (Fig. 1) and "sensitivity factors" (SF—peak area divided by corresponding hydrogen concentration, see Fig. 2) allows to evaluate H_2 concentration, the accuracy of such procedure is relatively low in comparison with other components of the reaction mixture: for instance, in the same conditions SF for oxygen is nearly constant in the whole range of concentrations and is about 80 times that of hydrogen at <10 vol.%.

Both sensitivity and accuracy of hydrogen detection sharply increase if we use argon as a carrier gas. In this case, hydrogen peaks have "normal" shape, their areas are proportional to hydrogen concentration and SF sharply increases due to a big difference in thermal conductivity between Ar and H_2. Unfortunately, in this case, for the same physical reason, SF values for all other components of the reaction mixture drastically drop. The second important factor decreasing SF values is that the conditions of safe usage of TCD do not allow to work at relatively high detector currents when Ar is used as a carrier gas.

At this point we have to conclude that the most reliable results in GC analysis of the reaction mixture can be obtained when two carrier gases are used in parallel: helium—for the rough estimation of hydrogen concentration and for the quantitative analysis of the rest of the mixture, and argon—to measure hydrogen concentration more precisely. This approach was used in our experiments.

To evaluate the efficiency of dehydrogenation process we used the following criteria:

1. Degree of equilibration (DE) calculated based on Eqs. (1) and (3) and on thermodynamic data given in [6] as follows:

$$\mathrm{DE} = \frac{[\mathrm{olefin}]_{\mathrm{ex}} \times [\mathrm{H}_2]_{\mathrm{ex}}}{K_{\mathrm{eq}}[\mathrm{alkane}]_{\mathrm{ex}}} \qquad (3')$$

   where $[\mathrm{olefin}]_{\mathrm{ex}}$, $[\mathrm{alkane}]_{\mathrm{ex}}$, $[\mathrm{H}_2]_{\mathrm{ex}}$ are the concentrations of olefin, initial alkane and hydrogen, respectively, obtained in the current experiment.

   By definition, the DE value shows how close the product concentrations are to those allowed by thermodynamics of the reaction (1′).

2. Relative efficiency degree (RED) calculated based on Eq. (2):

$$\mathrm{RED} \approx \frac{Y_{\mathrm{ex}}}{K_{\mathrm{eq}}^{0.5} P_0^{-0.5}} \qquad (4)$$

For any particular experiment it shows how close the yield of olefins is to the one allowed by thermodynamics at the same temperature and pressure. In principle, RED can be used as a measure of efficiency in both non-oxidative and oxidative transformation of alkanes into olefins. In the latter case, if the RED value is higher than 1 in ODH process, this would indicate that the target of using oxidative process is reached and olefin yield exceeds the equilibrium in NODH for the given temperature and pressure.

3. Results

3.1. Conversion of alkanes in the presence of oxygen

3.1.1. Effect of temperature

Experiments over a series of V- and Sb-based catalysts in a wide range of temperatures show that hydrogen forms as one of the major products, especially in the conditions in which catalysts display the highest performance in olefin production. Fig. 3 shows the trends in concentrations of some components of reaction mixture, propylene selectivity and RED at increasing temperature during propane oxidation over Sb-, V- and V-Sb-alumina catalysts. V-containing catalysts are much more efficient in olefin production displaying very similar profiles of the main reaction parameters versus temperature. It is interesting to note

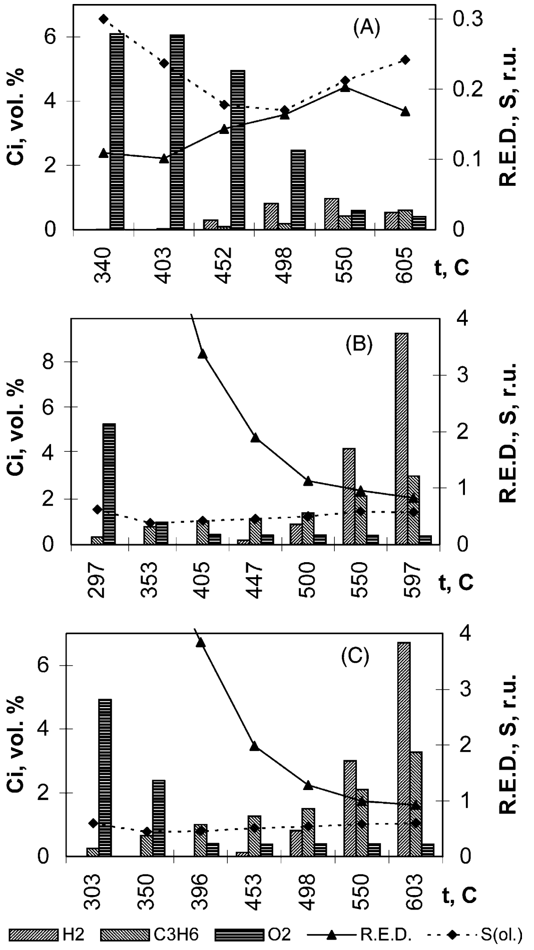

Fig. 3. Process parameters as functions of flow rate during propane oxidation over 0.6 g of supported Sb- (A), V- (B) and VSb-alumina (C) catalysts. Initial mixture: 17.3 vol.% C_3H_8 + 29.5 vol.% air in He, 10 ml/min.

that while over Sb-alumina catalyst propylene yields do not reach values allowed by thermodynamics at any temperatures (low RED values), both V-containing catalysts efficiently catalyze the ODH process, and at relatively low temperatures the RED values exceed 1 by far. However, at increasing temperatures despite the increasing propylene concentrations in the reaction mixture, the RED values decrease and become lower than 1. Simultaneously over these two catalysts hydrogen concentration becomes very high in the conditions of almost total consumption of oxygen from the reaction mixture. These facts may suggest that in these conditions a NODH process takes place. However, the analysis of product yields shows that even if NODH is the only process leading to the formation of olefin, hydrogen production exceeds by far the value corresponding to the formation of olefin and its possible sequential overoxidation.

As it was shown earlier [12], doping with antimony suppresses coke formation over V-alumina catalyst in the conditions of ODH. The higher production of hydrogen over V-alumina sample may also be indicative for the intense coking when oxygen is almost totally consumed. This assumption is in a good agreement with the results of catalyst reoxidation: if oxygen is supplied on the sample after catalytic tests, temperature jump is observed and CO_2 is detected in the gas phase. Its concentration is high in the case of V-alumina and almost negligible over Sb-containing catalysts.

On the other hand, the obtained data on hydrogen formation cannot be explained solely by anaerobic coking. First, over Sb-alumina hydrogen appears in the reaction mixture well before the total consumption of oxygen. Secondly, Sb-containing catalysts have very low coking activity, but both of them produce hydrogen.

In the case of ethane oxidation, the main features are very similar to those observed during propane oxidation over the same catalysts (see Fig. 4):

- hydrogen forms over all three catalysts in this series;
- its concentration increases sharply at rising temperature and at certain point exceeds olefin concentration;
- while over V-containing catalysts hydrogen appears in the reaction mixture at almost total conversion of oxygen, in the presence of Sb-alumina sample hydrogen-to-olefin ratio exceeds 1 even at high concentrations of oxygen.

As to the RED values, during ethane oxidation they also exceed 1 by far at relatively low temperatures and substantially decrease above 400 °C. However, in contrast to experiments with propane, even at 550 °C at almost total conversion of oxygen ethylene yields remain higher than those allowed by thermodynamics for NODH in the same conditions.

3.1.2. *Effect of flow rate*

Variations of reaction parameters depending on the flow rate were studied over the same catalysts in the

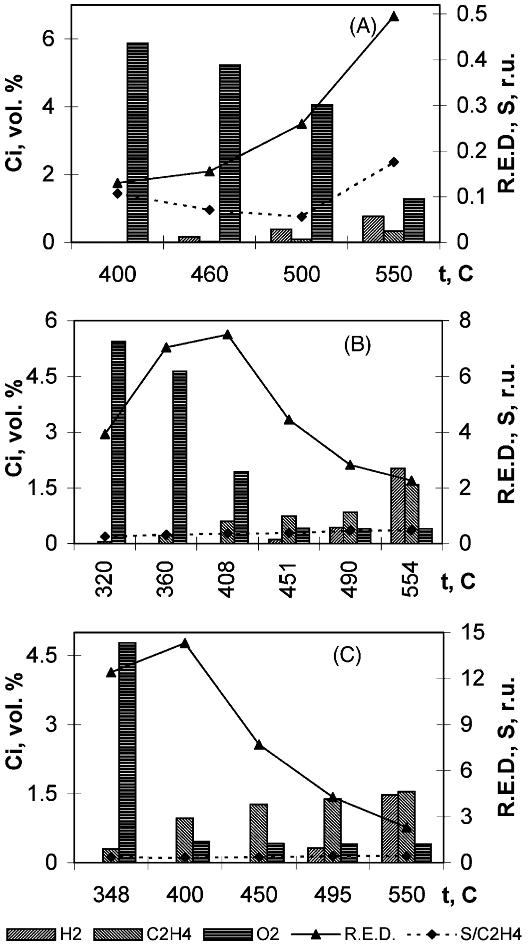

Fig. 4. Process parameters as functions of flow rate during ethane oxidation over 0.6 g of supported Sb- (A), V- (B) and VSb-alumina (C) catalysts. Initial mixture: 17.2 vol.% C_2H_6 + 29.5 vol.% air in He, 10 ml/min.

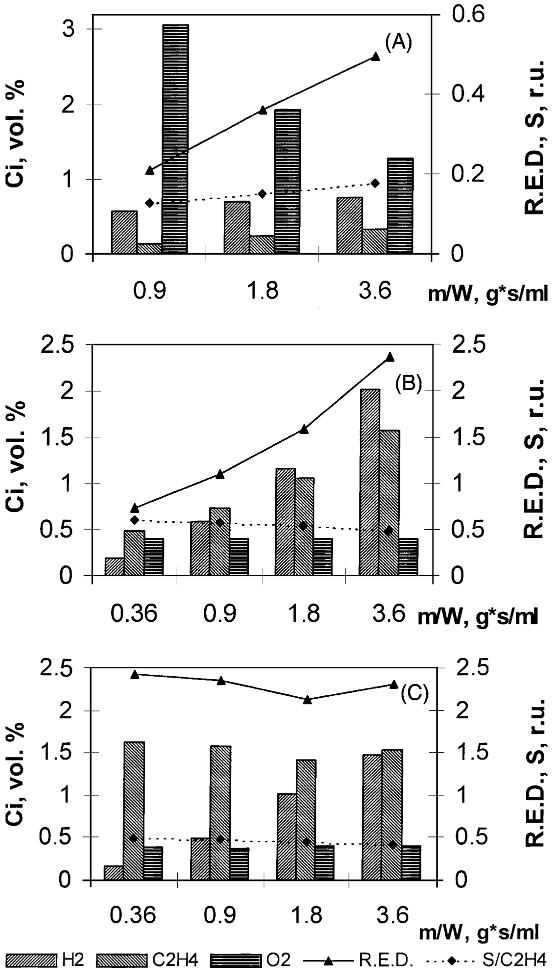

Fig. 5. Process parameters as functions of flow rate during ethane oxidation over supported Sb- (A), V- (B) and VSb-alumina (C) catalysts. Initial mixture: 17.2 vol.% C_2H_6 + 29.5 vol.% air in He, 550 °C.

conditions close to optimal production of olefins—at 550 °C and residence times varied between 0.36 and 3.6 s g/cm^3. As can be seen from Figs. 5 and 6, over less efficient Sb-alumina catalyst oxygen conversion and olefin concentrations increase with residence time. Hydrogen prevails over olefins in the whole range of residence times and undergoes much slighter changes, especially in the case of propane. Over more efficient V-containing systems variations in olefin concentrations are much less substantial, especially in the case of VSb/γ-Al_2O_3 catalyst. On the other hand, at increasing flow rates (or decreasing residence times) in the same range a much more pronounced drop in production of hydrogen is observed.

3.1.3. *Effect of alkane nature*

The above data shows that over more efficient V-containing catalysts at shorter residence times hydrogen concentrations undergo a stronger drop as compared with olefins. This is very likely indicative of decreasing contribution of NODH to olefin formation. Based on this, we carried our the experiments with a lower catalyst loading (0.025 g) in order to trace how the ODH efficiency varies depending on the

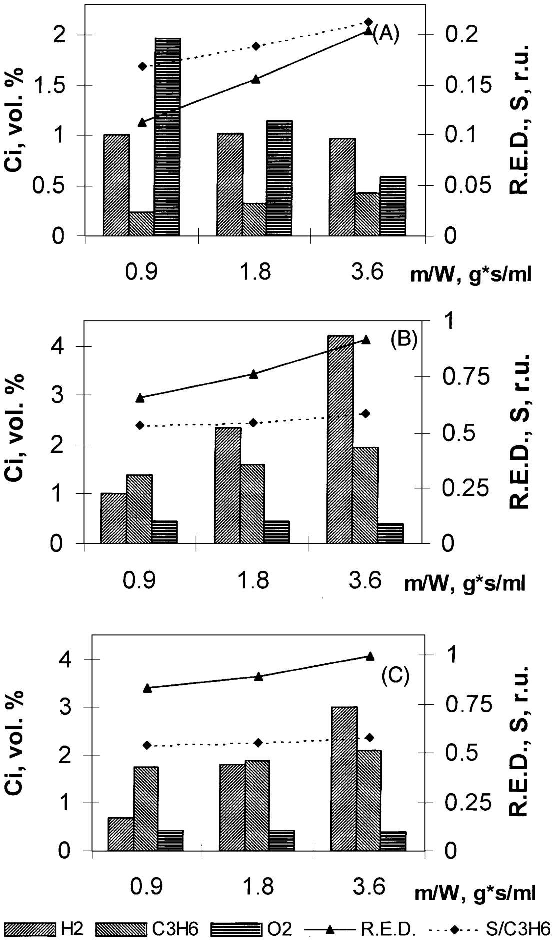

Fig. 6. Process parameters as functions of flow rate during propane oxidation over supported Sb- (A), V- (B) and VSb-alumina (C) catalysts. Initial mixture: 17.3 vol.% C_3H_8 + 29.5 vol.% air in He, 550 °C.

number of carbon atoms in the initial alkane molecule over the same catalyst in the same conditions. These experiments were performed over one of the most efficient ODH catalysts in V-alumina series—VSbBiBa/γ-Al_2O_3 (see [10,11]).

The comparison of data obtained with different alkanes (see Fig. 7) shows that both olefin concentrations and RED values decrease from ethane to *iso*-butane reflecting the fact that the difference in thermodynamic stability of initial molecules exceeds that in their reactivities. It is interesting to note that in spite of substantial drop in the RED value from ethane to *iso*-butane, hydrogen concentration in the reaction mixture sharply increases in this direction: it is below the detection limit in the case of ethane, reaches detectable, but low values in the case of propane and becomes comparable with *iso*-butene concentration in the case of *iso*-butane. This indicates that certain pathways of hydrogen formation become more important at increasing length of carbon chain in hydrocarbon molecules.

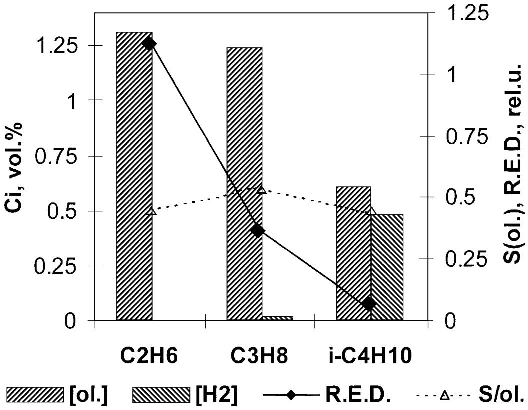

Fig. 7. Variation of process parameters in a series of C_2–C_4 alkanes at 600 °C (0.1 g s/ml; initial mixture: ~17% alkane + 30% air in He).

3.1.4. Effect of oxygen concentration

The results obtained over the VSbBiBa/γ-Al_2O_3 catalyst at varied initial oxygen concentration during *iso*-butane oxidation are presented in Fig. 8. As can

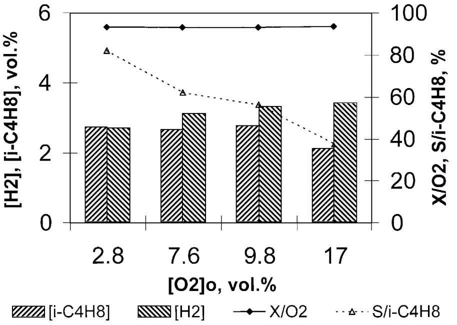

Fig. 8. Concentrations of *iso*-butene and hydrogen, oxygen conversion and *iso*-C_4H_8 selectivity as functions of initial oxygen concentration during oxidation of *iso*-butane over VSbBiBa-alumina catalyst: 0.6 g of catalyst; flow rate: 10 ml/min; initial *iso*-C_4H_{10} concentration: 15 vol.%; 550 °C.

be seen, in given conditions almost total conversion of oxygen is reached. Concentration of *iso*-butene in the reaction mixture decreases at increasing initial oxygen concentration at sharply rising concentrations of carbon oxides (*iso*-butene selectivity drops from 86 to 45%). This means that oxygen added to the initial mixture above some certain (relatively low) concentration is spent mainly on the formation of carbon oxides. The RED values in these conditions are low decreasing from 0.23 to 0.18 at initial oxygen concentration increasing from 2.8 to 17%.

As to hydrogen, its production gradually increases at increasing initial oxygen concentration. However, since at almost total oxygen conversion the DE value remains low (0.013–0.018), one may conclude that the process proceeds far from equilibrium and hydrogen is formed likely not in NODH, but via some other pathway which is stimulated by oxygen in some manner.

The trends described above are suggestive for an existence of multiple pathways for hydrogen formation in the conditions of alkane oxidation. These pathways should follow different kinetic regularities when reaction parameters, such as temperature, residence times and reactant concentrations, are varied.

3.2. *Anaerobic conditions*

As we demonstrated earlier [12], the VSbBiBa/γ-Al_2O_3 catalyst is able to efficiently supply active oxygen to produce olefins from alkanes in cyclic pulse redox regime. In this section, we present the data obtained in the absence of any oxidant in the feed gas when the flow of pure ethane is supplied at 550 °C on the VSbBiBa/γ-Al_2O_3 catalyst pre-oxidized in air flow. In these conditions, ethylene, carbon oxides and hydrogen are detected in the outlet gas, and their concentration are changing with time. The data on C_2H_4 and H_2 concentrations versus time-on-stream are presented in Fig. 9 along with DE values. On early stages of the process (time-on-stream <50 min) a substantial contribution of catalyst lattice oxygen leads to a partial burning of hydrocarbon that decreases the concentration of olefin and hydrogen. However, even during this period hydrogen concentration approaches to the equilibrium value much faster than ethylene. Over a reduced sample (time-on-stream >50 min) concentrations of ethylene and hydrogen become stable and nearly equal at DE ∼0.8. One may conclude that the reduced VSbBiBa/γ-Al_2O_3 behaves as an efficient NODH catalyst. If oxygen is present in the initial

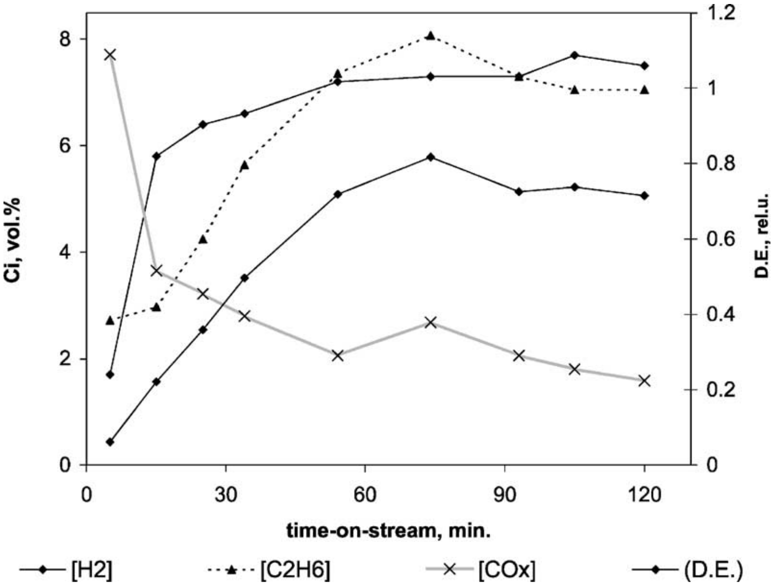

Fig. 9. Variations in product concentrations and DE values with time-on-stream during anaerobic conversion of ethane over pre-oxidized VSbBiBa/γ-Al_2O_3 catalyst at 550 °C; ethane flow 0.1 ml/s g.

mixture, but its conversion is high, the conditions similar to the experiment presented in Fig. 9 can set up in the substantial part of the catalyst bed where the NODH process can proceed.

4. Discussion

To summarize the above experimental data, hydrogen formation is not an exception, but a general phenomenon taking place during light alkane oxidation in the presence of typical ODH catalysts. The analysis of this phenomenon is very important for better understanding the chemical nature of the overall process. Moreover, since the highest concentrations of hydrogen in the reaction mixture are observed in the conditions close to optimal olefin formation, the elucidation of the process pathways is worth for further optimization of target product yield. In fact, one possibility is that a substantial fraction of olefin forms simultaneously with H_2 via NODH over reduced catalyst at the expense of heat produced in total oxidation reaction (in which the most part of oxygen is consumed). If so, there is no practical reason to run the reaction in the oxidative mode and a more economical way to supply heat for NODH should be found. On the other hand, if hydrogen formation is a result of some by-processes, special efforts should be mounted to suppress them. In the latter case, monitoring of H_2 concentration in the reaction mixture is a good way to control the efficiency of these efforts.

Unfortunately, as we noticed in Section 1, in most of the experimental studies dealing with ODH of light alkanes concentration of hydrogen is not measured. Paper [13] devoted to ethane ODH over Cr- and Pt-containing catalysts at short (millisecond) contact times is an exception from this rule. Analyzing temperature excursions and product distributions at varied catalyst formulations and reaction conditions, authors arrived to the following conclusion: efficient supported Cr_2O_3 catalyst acts essentially as two catalysts in two reaction environments. In the oxidizing environment near the reactor inlet it behaves as relatively active and selective ODH catalyst. The major part of oxygen is consumed on this stage. In the remaining part of the catalyst a NODH proceeds in the absence of oxygen at the expense of the heat generated by the highly exothermic oxidation reactions at the front part of the catalyst.

Although we agree that such scheme can be applied also to our experiments, it cannot, however, explain some of our observations, e.g. RED values exceeding 1 (in experiments with ethane) and hydrogen concentrations exceeding concentrations of olefins.

High concentrations of hydrogen over V-alumina catalyst are likely formed at the expense of coking. In the presence of Sb-containing catalysts, however, this pathway can be neglected.

As we demonstrated earlier [10], free-radical gas-phase processes play a very important role in product formation during light alkane oxidation over V-containing supported catalysts, including those studied in this work. The development of chain process in the gas phase leads to the formation of various radical and molecular species further transformations of which can produce hydrogen. First of all, alkyl radicals C_nH_{2n+1} formed as primary radical species during alkane activation in heterogeneous or homogeneous steps can undergo consecutive scission evolving H-atom which then reacts with any H-containing molecules RH (first of all, with initial alkane) with H_2 molecule formation:

$$[O]_S + C_nH_{2n+2} \rightarrow [OH]_S + C_nH_{2n+1} \qquad (2')$$

$$X + C_nH_{2n+2} \rightarrow XH + C_nH_{2n+1} \qquad (3'')$$

$$C_nH_{2n+1} \rightarrow H + C_nH_{2n} \qquad (4')$$

$$RH + H \rightarrow R + H_2 \qquad (5)$$

where $[O]_S$ is the active surface site; X is any gas particle which has an affinity to hydrogen atom (e.g. O_2, OH, HO_2, H, alkyl, alkoxy, alkylperoxy species, etc.).

As can be seen, the sequence of steps (2′), (4′) and (5) leading to the formation of at least one olefin and one H_2 molecules and to the development of homogeneous chain process starts from the oxidative abstraction of H-atom from alkane molecule by a surface active site. If a chain initiation takes place in the gas phase, the first step (3″) (in this case $X = O_2$) is also an oxidative H-atom abstraction. The same can be said about alkane molecule reaction (3″) with any oxidative particles present in the gas phase during a developed chain reaction. In other words, this sequence of steps can be considered as an oxidative process leading to molecular hydrogen forming in parallel with olefin.

Besides that, substantial amounts of H-atoms participating in step (5) are formed in decomposition of CHO radicals

$$\mathrm{CHO \rightarrow CO + H} \quad (6)$$

which, in their turn, are formed in reactions of aldehydes

$$\mathrm{RCHO \rightarrow R + CHO} \quad (7)$$

or

$$\mathrm{HCHO + X \rightarrow XH + CHO} \quad (8)$$

In our work dedicated to the OCM process [9] we explained the formation of high concentrations of molecular hydrogen during methane oxidation at moderate temperatures (below 650 °C) by the formation and rapid decomposition of formaldehyde. It is worth to note that this temperature range corresponds to that in which an efficient catalytic ODH of light alkanes takes place. Modeling of catalytic heterogeneous–homogeneous oxidation of methane [14] shows that the sequence of steps (8) ($X = O_2$), (6) and (5) ($RH = CH_4$) is the main route of molecular hydrogen formation in this complex process. On the other hand, the probability of step (2′) is very high in the typical ODH conditions [15], and it is known that formaldehyde forms as one of main products during gas-phase oxidation of any hydrocarbon. As a result, the route which includes steps (7), (8), (6) and those preceding the formation of aldehydes can be considered as an important oxidative pathway of hydrogen formation.

Although homogeneous pathways discussed above are highly probable, additional experimental and modeling studies are required to evaluate their contribution quantitatively.

5. Conclusions

In the conditions of optimal production of olefins during oxidation of light alkanes over typical ODH catalysts molecular hydrogen forms as one of the major products. Variations of kinetic features depending on the initial alkane, catalyst and reaction conditions are indicative for the existence of multiple pathways of hydrogen formation.

If almost total conversion of oxygen takes place in the front part of the reactor, NODH process can proceed in the remaining part of catalyst bed. Over some catalysts (e.g. V/γ-Al_2O_3) hydrogen formation can also accompany the intense coking.

In addition to non-oxidative routes, some oxidative processes, including those proceeding in the gas phase, can lead to the production of hydrogen which in this case is accompanied by both additional olefin formation and total oxidation.

Further elucidation of the reaction pathways can help to improve the target olefin production.

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