# Radical Generation during Pyrolysis of $n$-Undecane on BaCl$_2$ and Imperfect Magnesium Oxides

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## Abstract

The kinetics of ethyl radical generation during the pyrolysis of $n$-undecane on barium chloride (accelerating the heterogeneous constituent of the process) and on defect-bearing magnesium oxides (accelerating the homogeneous constituent of the process) was investigated by means of freezing out in the cavity of the EPR spectrometer. It was shown that the activation energy of radical generation on barium chloride ($E$ = 192 kJ/mol) is lower than the activation energy of thermal pyrolysis ($E$ = 322 kJ/mol). The phenomenon of ignition of the surface is observed with the catalysts that accelerate the homogeneous constituent of the process and create the «catalysis sphere.» Below the critical temperature, in spite of the presence of catalysts, ordinary thermal pyrolysis goes on between the catalyst granules. At a higher temperature, the catalyst generates radicals with the activation energy characteristic of the radical reactions ($E$ = 4 kJ/mol). The possibility to increase the productivity and to control the selectivity of pyrolysis of hydrocarbons by including non-conventional heterogeneous catalysts into the process is demonstrated.

## INTRODUCTION

Pyrolysis of hydrocarbons is the most large-scale process of refining of high-gravity oil, natural gas and once-run petrol. This process gives a range of valuable products and semi-products for petrochemical, varnish-and-paint, pharmaceutical industry and for fine organic synthesis. The main products of pyrolysis are α-olefin hydrocarbons, C$_2$ and higher, dienes, light-weighed aromatic compounds. In industry, pyrolysis of hydrocarbons is carried out at a temperature of 800−1200 °C, which determines high energy consumption in this process. High temperature also promotes an increase in the contribution from by-processes of coking and resinification, synthesis of condensed naphthenes and aromatics which do not find practical application at present and cause pollution of the environment. Pyrolysis of hydrocarbons proceeds *via* the non-branched radical chain mechanism, so the selectivity of

the process towards one or another useful product defies control. The listed shortcomings initiate the search for alternative methods of pyrolysis. Among them, catalytic pyrolysis is distinguished. With the use of catalysts, it will be possible to reduce temperature and to make the process more flexible with respect to the initial raw material and to the groups of final products, taking into account the variable market conditions. The data published in this area are enormous and empirical. Researchers just sort out all the possible combinations of oxides and supported metals as catalysts of pyrolysis, thus trying to get the keys to the basic process of petrochemistry as soon as possible. Analysis of the published works proves that the efficiency of the catalysts used for this process is insignificant. In our opinion, the reason is that the mechanism of catalytic action and the regularities of conventional heterogeneous catalysis are always mechanically transferred to the case of pyrolysis with the

participation of catalysts. It is clear that the problem would not be solved without thorough investigation of the mechanism of action of the catalyst surface on non-branched radical chain processes (RBP). Meanwhile, the fundamental research in this area can promote principally novel solution of this problem by realizing the pyrolysis process with the participation of catalysts.

## BASIC FOUNDATIONS OF THE MECHANISM OF CATALYTIC RADICAL BRANCHED PROCESSES

Our investigations [1–5] revealed the mechanism by which the heterogeneous catalysts participate in the RBP of hydrocarbon pyrolysis. Ordinary thermal pyrolysis, the mechanism of which had been established as long ago as in the early 1930s, proceeds in the gas phase. It consists of three stages.
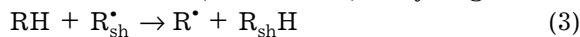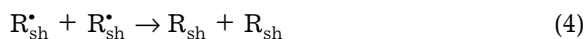
I. Initiation, or formation of radicals:

$$R-R_{sh} \rightarrow R^{\cdot} + R_{sh}^{\cdot} \tag{1}$$

II. Chain propagation:

decomposition of long-chain radicals

$$R^{\cdot} \rightarrow R_{sh}^{\cdot} + \alpha\text{-olefins} \tag{2}$$

detachment (substitution) of hydrogen atoms

$$RH + R_{sh}^{\cdot} \rightarrow R^{\cdot} + R_{sh}H \tag{3}$$

III. Chain termination, or radical recombination:

$$R_{sh}^{\cdot} + R_{sh}^{\cdot} \rightarrow R_{sh} + R_{sh} \tag{4}$$

Here $R_{sh}^{\cdot}$ are short-chain radicals carrying on the chain process $CH_3^{\cdot}$, $C_2H_5^{\cdot}$, $H^{\cdot}$; $R^{\cdot}$ are long-chain radicals; RH, $R_{sh}R_{sh}$, $R_{sh}H$ are the molecules of alkanes. In reality, each of the reactions (1)–(4) is a set of several elementary steps participated by the molecules and radicals of diverse structures. Reaction (3) is a limiting reaction of chain propagation. The composition of the target products is formed by the chain propagation reactions (2), (3). Since the chain length of hydrocarbon pyrolysis is close to unity and the rates of reactions (1) and (3) are quite comparable, the total rate $W_T$ of the thermal process is $W_T = V_1 + V_3$.

We demonstrated that in the presence of catalysts, along with homogeneous reactions (1)–(4), also the heterogeneous continuation of the chains is possible through the surface active centres (a.c.) designated as S:

$$S + RR_{sh} \rightarrow SR_{sh} + R^{\cdot} \tag{5}$$
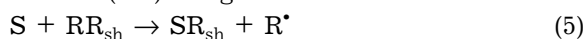
and regeneration of a.c.:

$$SR_{sh} + R_{sh}^{\cdot} \rightarrow S + R_{sh}R_{sh} \tag{6}$$
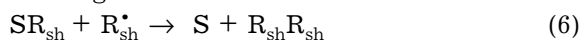
Active centres S are of radical nature. A sequence of reactions (5), (6), (5), (6), (5) ... can be considered as the heterogeneous chain propagation. In a real process, it is impossible to separate the homogeneous and heterogeneous constituents of the process since the chains may propagate *via* random routes including both homogeneous a.c. $R_{sh}^{\cdot}$ and heterogeneous ones S. For example, (1), (6), (5), (2), (3), ....(4) or (1), (3), (2), (6), (5), ....(6), *etc*. Hydrocarbon pyrolysis participated by catalysts is classified as a heterogeneous-homogeneous process. Total process rate is $W_S = V_1 + V_3' + V_5$ if the limiting stage of heterogeneous chain propagation is reaction (5) rather than reaction (6). So, the process rate is a sum of the homogeneous constituent of the process $V_1 + V_3'$ and the heterogeneous constituent $V_5$. The rate of the homogeneous chain propagation $V_3'$ in the presence of a catalyst may be substantially different from $V_3$ for the case of thermal pyrolysis.

It was shown that the reactivity of a.c. S is determined by their ability to form the surface compounds with hydrocarbon radicals $R_{sh}^{\cdot}$; these compounds are characterized by a definite bond energy $D_{S-R}$. Depending on the reactivity of a.c. S, four types of the action of surface on the process are possible: inhibitive, neutral, accelerating the heterogeneous constituent, or accelerating the homogeneous constituent of the process [1]. The catalytic action is possible if $D_{S-R}$ values are comparable with bond energy values $D_{C-C}$ in the molecules undergoing pyrolysis [2].

It was shown theoretically [1, 2] that if a catalyst accelerates the heterogeneous constituent of the process, the conversion level of the initial hydrocarbon is determined mainly by the concentration of heterogeneous a.c. S per unit reaction volume. Reactions (1)–(4) proceed in the gas phase, but chain propagation is due to reactions (5), (6) which are more energy-profitable. Among the surface reactions, the limiting one is (5), and $[S] \gg [R_{sh}]$. In this case, the steady concentration of hydrocarbon radicals is lower than or equal to the concentration of radicals during thermal pyrolysis under similar conditions, that is,

without a catalyst [1, 2]. The chain process develops mainly with the participation of radical a.c. S. The acceleration of the heterogeneous constituent can be observed for $320 \text{ kJ/mol} > D_{\text{S}-\text{R}} > 180 \text{ kJ/mol}$. In this case, all reactions (1)−(6) proceed in the reaction volume, but the overall rate of the process is determined by the heterogeneous continuation and $W_{\text{S}} \approx V_5$. During pyrolysis of individual hydrocarbons on the catalysts of this kind (atmospheric pressure, $T = 650-720$ °C), while total transformation degree increases, the overall content of light-weighed $C_1-C_4$ alkanes and hydrogen in the products of pyrolysis is the same as that in the products of thermal pyrolysis. These compounds are formed as a result of the reactions of chain propagation and radical recombination. They are not target products, but their formation is an indirect evidence of the concentrations and transformation routes of the radicals that drive the chain process.

If the presence of the catalyst accelerates the homogeneous constituent of the process, the steady concentration of radicals will be higher than that in the case of thermal pyrolysis under similar conditions [1, 2]. The limiting reaction of the heterogeneous chain propagation is reaction (6) and [R$_{\text{sh}}$] >> [S]. The level of hydrocarbon conversion is determined by the concentration of homogeneous a.c. R$_{\text{sh}}^{\bullet}$ and the homogeneous chain propagation, $W_{\text{S}} \approx V_3'$. In this case, the role of the catalyst is the generation of an additional amount of the radicals driving the chain process. Experimentally, not only an increase in the rate of the process is observed but also an increase in total content of light-weighed alkane fractions and hydrogen in the products as compared to the composition of the products of thermal or catalytic pyrolysis, if the catalyst accelerates the heterogeneous constituent [2].

We demonstrated [4] that an increased concentration of radicals is formed only in the gas phase layer near the surface. The space with increased concentration of radicals was defined as the catalysis sphere. The dimensions of this sphere under typical conditions of pyrolysis were estimated theoretically [4]. The radicals generated by the catalyst surface penetrate into the gas phase at a depth of several tens of a

millimeter. In the rest of the gas space between the catalyst granules, usual thermal pyrolysis takes place, that is, the effect of the catalyst is insignificant. This means that the reactor geometry, catalyst texture, methods of its arrangement in the reactor and the linear rates of reaction flow for hydrocarbon pyrolysis under real conditions should be calculated taking into account the formation of the sphere and its maximal efficiency factor.

Taking into account the practical and fundamental significance of the «sphere» phenomenon, we obtained a direct experimental confirmation of the existence of the sphere. Investigation of the overall generation of radicals during the pyrolysis of *n*-undecane on different catalysts was carried out by freezing the radicals out in the resonator of the EPR spectrometer [5]. It was shown that in the case of the most active pyrolysis catalysts the amount of the radicals frozen out is almost an order of magnitude larger than that in the case of thermal pyrolysis under similar conditions.

The investigation procedure was developed and the kinetics of generation of ethyl radicals during the pyrolysis of *n*-undecane under thermal conditions on quartz granules that were inert towards pyrolysis and on the granules of commercial magnesium oxide was investigated [6]. It was shown that both on the inert quartz and in the case of thermal pyrolysis (when there are no granules) the rates of radical generation are almost identical. During the pyrolysis on MgO granules, up to a definite temperature point, the activation energy value ($E = 322 \text{ kJ/mol}$) is the evidence that, in spite of the presence of MgO in the reactor, usual thermal generation of the radicals takes place in the reactor. Above the critical temperature point, activation energy decreases at once to $E = 62.8 \text{ kJ/mol}$. The surface of the oxide is kind of flamed up and generates radicals with activation energy more typical for radical reactions. A question arises whether such a behaviour of the catalysts of hydrocarbon pyrolysis is typical.

The goal of the present work is to investigate the kinetics of radical generation by the catalysts that accelerate mainly either the heterogeneous or homogeneous constituent of pyrolysis process. The choice of the catalytic

systems was carried out on the basis of the data on the conversion and yield of light-weighed alkanes $C_1-C_4$ and hydrogen as obtained in the investigation of the activity of catalysts directly in the pyrolysis of individual hydrocarbons under the conditions close to the industrial ones (atmospheric pressure, $T = 650-750$ °C). Commercial barium chloride of reagent grade was investigated as a typical catalyst accelerating the heterogeneous constituent of the process; while the catalysts accelerating the homogeneous constituent were the most active synthesized defect-bearing magnesium oxides [7, 8] and commercial MgO (reagent grade). The commercial $n$-undecane of the pure reagent grade (pure grade) was used as the reagent.

## EXPERIMENTAL

Defect-bearing magnesium oxides were obtained by hydration of the initial reactive oxide in strong solutions of magnesium acetate or nitrate, followed by drying and calcination. The samples were marked as $MgO/MgAc_2$ and $MgO/Mg(NO_3)$ catalysts. The mechanism of formation of defect-bearing oxides was established; this method of synthesis involves epitaxial broadening of the oxygen framework of magnesium oxide due to oxygen atoms of acetate or nitrate groups. In this process, some oxygen octahedra of defect-bearing oxide contain the anion residues with a positive charge different from 2+ instead of the central magnesium cation [9, 10]. So, defect-bearing magnesium oxides are unusual substitution solid solutions. The structural and charge heterogeneities are conserved during long-term calcination of the samples even at 1000 °C in the air and after the tests of hydrogen pyrolysis for many hours.

The kinetics of reactions of radical generation was investigated with a vacuum set-up composed of the units of hydrocarbon pyrolysis and transport of the resulting radicals into the unit of freezing them out into an extension of Dewar vessel which was placed in the resonator of the EPR spectrometer. The Dewar vessel was cooled with liquid nitrogen. A schematic of the vacuum set-up, the dimensions of the reactor with a grate for catalyst granules, and the conditions of recording the spectra of ethyl radicals were described elsewhere [6]. The vapour of $n$-undecane purified preliminarily from the traces of oxygen and moisture was subjected to pyrolysis. The reactor was charged with 20 granules of quartz or of the catalyst (the size of granules was ~1.2 mm). Time of the contact between the hydrocarbon and the catalyst t for $T = 923$ K was $5 \cdot 10^{-4}$ s. Before each run, the reactor was evacuated at 1023 K and $P = 10^{-4}$ Torr for 2 h. At a temperature of 600 K in the reactor, a matrix was formed from undecane vapour in the extension of the Dewar vessel; ethyl radicals were later frozen out onto this matrix. Methyl radicals and hydrogen atoms are not frozen out under the indicated conditions, though they are present in comparable amounts. After the formation of the matrix, the set-up was evacuated again; temperature was risen up to the necessary point. When measuring the rate of accumulation of ethyl radicals, $n$-undecane was supplied and the spectrum was recorded continuously. The rate of radical accumulation was measured within temperature range 873–953 K. All the operations were time-standardized.

The proposed procedure allowed us to measure correctly the rate of generation of ethyl radicals. Estimation showed that less than 2 % of the generated radicals were consumed in chain propagation reactions (reactions with undecane molecules). Under the experimental conditions, the contribution from the volume and surface processes of radical recombination and the reactions of long-chain radical decomposition can be neglected [6].

## RESULTS AND DISCUSSION

For undecane pyrolysis on 20 granules of barium chloride, which is known to accelerate the heterogeneous constituent of the process, the Arrhenius plot (Fig. 1) exhibits a straight dependence of the logarithm of radical generation rate on inverse temperature. The same dependence is observed for thermal pyrolysis and for pyrolysis on quartz (see Fig. 1). However, the activation energy of radical generation during thermal pyrolysis is
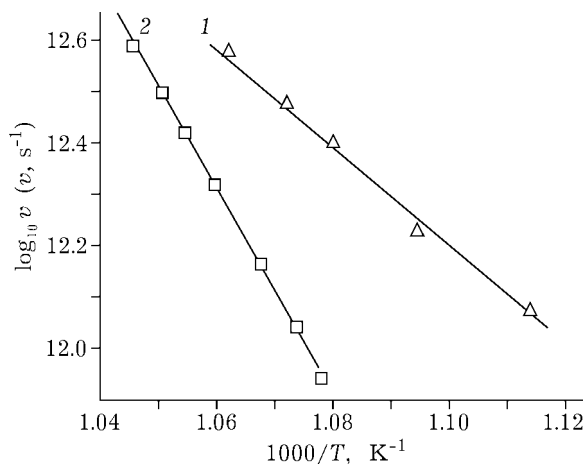
Fig. 1. Dependence of the logarithm of the radical generation rate on inverse temperature for pyrolysis of *n*-undecane on barium chloride (*1*) and quartz (*2*).
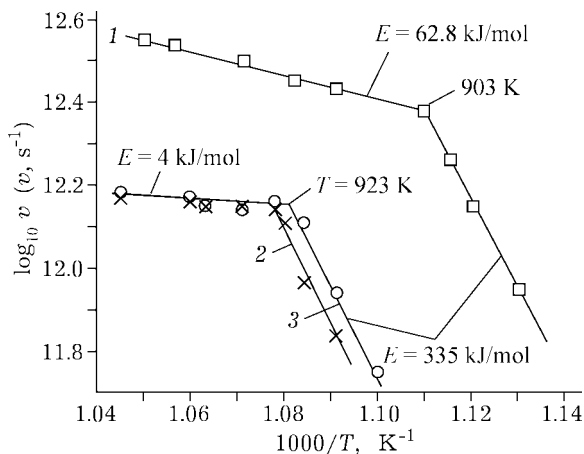
Fig. 2. Dependence of the logarithm of the radical generation rate on inverse temperature for pyrolysis of *n*-undecane on magnesium oxide (and defect-bearing magnesium oxides): *1* − MgO, *2* − MgO/MgAc₂, *3* − MgO/Mg(NO₃)₂.

$E = 322$ kJ/mol, while for barium chloride it is much lower and equals to 192 kJ/mol. It is evident that barium chloride catalyses the process.

For pyrolysis of *n*-undecane on 20 granules of defect-bearing magnesium oxides (MgO/MgAc₂ and MgO/Mg(NO₃)₂), curves with sharp bends are observed on the Arrhenius plots (Fig. 2). One can see that up to a definite temperature point in the reactor, despite the presence of catalyst granules, thermal pyrolysis proceeds with high characteristic activation energy. Above the critical temperature, the activation energy drops sharply down to the level characteristic of radical reactions. For magnesium oxide, $E = 62.8$ kJ/mol. For defect-bearing magnesium oxides the energy $E = 4$ kJ/mol is an evidence of the high activity of the surface a.c., which is characteristic more of atoms than of radicals.

Unlike BaCl, magnesium oxide and the defect-bearing oxides accelerate the homogeneous constituent of the process. One may assume that the appearance of the dependences with a sharp bend is characteristic only of the catalysts that are able to create a "sphere", that is, to generate additional radicals. The surface ignition effect is observed only for these catalysts.

Attention should be paid to the fact that the amount of the ethyl radicals generated on defect-bearing magnesium oxides is smaller than

that on MgO. Therefore, catalysts may possess not only different activity in radical generation but also different selectivity towards the nature of the generated radicals. In the case when hydrocarbons were subjected to pyrolysis under atmospheric pressure, an increased amount of hydrogen was observed in the products formed on defect-bearing oxides in comparison with thermal pyrolysis and pyrolysis on MgO [7, 8]. It may be assumed that under our experimental conditions (low pressure), too, the content of hydrogen atoms will be higher. As a consequence, the absolute amount of ethyl radicals frozen out will decrease. A similar picture is also characteristic of quartz and barium chloride.

It was noticed in theoretical analysis of the mechanism of RCP with the participation of heterogeneous catalysts that the higher the bond energy of the surface a.c. with a hydrocarbon radical $D_{S-R}$, the higher the probability for the reaction to pass from the surface into the gas volume [2, 4, 11]. Using activation energies of radical generation determined experimentally, one may verify the correctness of the phenomenological RCP model under development by us. Knowing the activation energy of radical generation (reaction (5)) and the C−C (or C−H) bond energy in hydrocarbon molecules (reference data) and using Polyanyi-Semenov's rule, one may estimate $D_{S-R}$ values for active S centres of the catalysts under

investigation. The corresponding values are listed below:

|            | $E$, kJ/mol | $D_{S-R}$, kJ/mol |
|------------|-------------|-------------------|
| Quartz     | 335         | –                 |
| BaCl$_2$   | 192         | 200               |
| MgO        | 62.8        | 360               |
| MgO$_{def}$ | 40         | 480               |

Indeed, the larger the $D_{S-R}$, the higher the probability for the catalyst to accelerate the homogeneous constituent of the process and creates the catalysis sphere. For MgO, $D_{S-R}$ values are close to the C−C bond energy; for defect-bearing magnesium oxides they are close to the C−H bond energy in hydrocarbon molecules. For barium chloride, $D_{S-R}$ values are smaller and correspond to the values for catalysts accelerating the heterogeneous constituent of RCP.

Analysing the results obtained, one may conclude that the a.c. on the catalysts accelerating the heterogeneous constituent of the process (see Fig. 1) eternally participate in radical generation process within the entire temperature range of pyrolysis. We suppose that the temperature of pyrolysis of these catalysts can be reduced until thermodynamic limitations for the yield of the target products (α-olefin hydrocarbons) come into force. Depending on the nature of hydrocarbons, the lower limit is $T = 470–550\,°C$. Under usual conditions of pyrolysis on these catalysts, the process rate should be directly proportional to the specific surface of the catalyst because it is proportional to [S]. However, it should be kept in mind that even in the case of acceleration of the heterogeneous constituent of catalytic RCP the gas-phase constituent is always present. A radical, once generated on the surface, is to have enough time to react (a long-chain radical is to decompose giving rise to α-olefins) in the gas volume before being consumed on the pore wall. Pore diameter or the distance between the grain surface or the surface of channels of catalyst blocks should be comparable to doubled free path of the formed radicals. Under atmospheric pressure and $T = 923\,K$, average $\lambda \geq 1000\,\text{Å}$ for radicals; thus, the pore diameter should be larger than 2000 Å. This requirement imposes limitations on texture; so, only the catalysts with large pores can be used. However, in this case, the specific surface and the contribution of the catalyst decrease. So, limitations in the catalytic action and the limits of temperature decrease can be due not only to the activity of specific catalysts but also to the required heterogeneity factor $S/V$ (the ratio of catalyst surface to the free gas volume).

The catalysts accelerating the homogeneous constituent of the process look more promising. A sphere with increased concentration of radicals is created above the surface a.c. S. Estimation shows that the concentration of S per unit reaction volume should be optimal: not very high (otherwise overlap of the spheres will cause an increase in the contribution from radical recombination reactions [4, 5]) and not very low (otherwise the contribution from the catalyst will be small, which will cause a decrease in the efficiency of the sphere and in the selectivity towards the target products). In the case of catalysts accelerating the homogeneous constituent of the process, the optimal value of the heterogeneity factor $S/V$ is determined by the activity of the catalyst, size of granules and the method of their arrangement within the reactor.

The surface "ignition" effect (see Fig. 2) is observed only with these catalysts and provides evidence that the reaction system (RCP as catalyst) is to overcome the potential barrier, after which the a.c. S appear on the surface; they have radical nature and are able to drive the chain process. Let us consider the factors that make the surface "ignite": temperature and radical concentration in the volume.

At high temperatures, coordinationally unsaturated oxygen forms having radical nature and being able to play the part of a.c. are formed on the surface of oxides as a result of desorption of the surface hydroxyl groups and carbonates [11]. In addition, the charge non-homogeneity conditioned by micro-impurities, for example, in the structure of commercial magnesium oxide at increased pressure may promote single-electron transitions with the formation of electron-hole pairs and emergence of one-electron centres on the surface. They may serve as active centres able to initiate generation of radicals (reaction (5)). Specially created charge non-homogeneity in defect-bearing magnesium oxides simplifies this process.

In addition to temperature, the electron state of the lattice of oxide catalysts may be substantially affected by radical reactions on its surface: adsorption and recombination of the radicals that were formed in thermal pyrolysis in the gas volume between the catalyst granules. It is worth mentioning that a substantial amount of energy equal to $D_{S-R}$ is released as a result of radical adsorption on a.c. S (see p. 666). The oxide crystal can accumulate a substantial part of this energy [6]. We suppose that under the conditions of temperature rise and an increase in the concentration of radicals to be adsorbed due to thermal pyrolysis, a moment can occur when the absorbed energy becomes sufficient for the electron-hole centres to be generated and to maintain the electron structure of the crystal in the non-equilibrium state. In this process, a.c. S with high energy potential having the radical nature are formed on the surface; this is the so-called ignition moment. Due to the surface reactions, the catalyst feeds its activity energetically. So, the steady concentration of S is due to two fast processes: single-electron transfer inside the crystal and single-electron transfer between the surface and the gas phase (reactions (5), (6)).

For the catalysts accelerating the homogeneous constituent, a critical temperature point exists below which they are inert with respect to RCP, though thermodynamic limitation is not reached yet and usual thermal pyrolysis goes on between the granules. Above the critical temperature point, the catalysts are active; they generate additional amount of radicals thus creating the catalysis sphere. Limitations for the catalysts creating the sphere involve "ignition" temperature and optimal heterogeneity factor taking into account the size of sphere.

In the area of classical heterogeneous catalysis, a.c. is of a definite chemical nature, while the rest part of the catalyst is just a support for a.c. For the RCP catalysts, the chemical nature and electronic structure of the entire catalyst crystal is important. It is necessary to develop research in the area opening new routes in foreseeing the catalytic action of substances in RCP.

**CONCLUSION**

According to the proposed mechanism of hydrocarbon pyrolysis participated by heterogeneous catalysts and the phenomenological model describing this process, two types of the catalytic action of the surface on the radical chain process are possible. The catalysts may accelerate either the heterogeneous or homogeneous constituent of the process. In the present work, a direct experimental confirmation of the existence of these catalysts is obtained. Their features were revealed and the directions of further research of the catalytic action of substances on RCP are formulated.

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