Theoretical Concept of Nonbranched Radical-Chain Reactions Involving Catalysts

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Abstract—The foundations of the theoretical concept of nonbranched radical-chain reactions involving heterogeneous catalysts are considered for hydrocarbon pyrolysis. These include the phenomenological model and the concept of the "catalysis sphere." Surface active sites S participate in chain propagation along with hydrocarbon radicals $R^•$ from the gas phase. Surfaces show either inhibiting or neutral action depending on the E_{S-R} bond energy. If the E_{S-R} value is comparable with the energy of the breaking bond in the reacting molecule, the reaction accelerates due to the acceleration of either the heterogeneous or homogeneous component of the overall rate of the process. In the latter case, the catalyst ensures the generation of additional radicals for the gas phase, which result in the formation of a catalysis sphere. The catalysis sphere is defined, the radical distribution in it is presented, and its properties and role in radical-chain processes are discussed.

INTRODUCTION

Since the discovery of radical-chain reactions, special attention has been given to the influence of the surface on their development. For example, the effect of the surface on the generation and decay of radicals has long been established for branched chain processes. Recently [1–4], surface active sites have been shown to participate in chain propagation and branching as adsorbed atoms or radicals and to affect the ignition limits of the reaction mixture [1–4]. In the papers devoted to nonbranched chain reactions, the surface has long been considered to exhibit no effect on chain propagation. Only in the past 20 years, many researchers have observed the catalytic action of the surface, for example, on hydrocarbon pyrolysis. However, they only reported facts and did not consider the mechanism for the surface action on nonbranched radical-chain processes.

In our previous studies of hydrocarbon pyrolysis on heterogeneous catalysts [5–11], we determined the mechanism of radical-chain processes with their participation. In the presence of catalysts, the heterogeneous chain propagation involving active sites of the surface takes place along with the homogeneous one. A phenomenological model of the catalytic pyrolysis of hydrocarbons was proposed, which comprised a system of kinetic equations describing both the homogeneous and heterogeneous stages of the process. The aim of this paper is to discuss possible catalytic radical-chain processes and to consider the "catalysis sphere," which is one of the most interesting phenomena in nonbranched radical-chain processes involving catalysts.

Thermal pyrolysis of hydrocarbons occurs by the nonbranched radical-chain mechanism consisting of three steps:
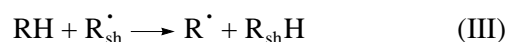
Initiation or radical (chain) generation

$$R - R_{sh} \longrightarrow R^• + R_{sh}^•. \qquad (I)$$

Chain propagation

$$R^• \longrightarrow R_{sh}^• + \alpha\text{-olefins} \qquad (II)$$

(the decomposition of long-chain radicals),

$$RH + R_{sh}^• \longrightarrow R^• + R_{sh}H \qquad (III)$$

(hydrogen atom abstraction), and
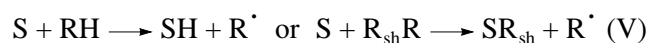
Chain termination

$$R_{sh}^• + R_{sh}^• \longrightarrow R_{sh}R_{sh} \qquad (IV)$$

(radical recombination).

In this scheme, $R_{sh}^•$ stands for short radicals acting as chain carriers ($CH_3^•$, $C_2H_5^•$, or $H^•$); $R^•$ represents long-chain radicals; and RH, $R_{sh}R_{sh}$, and $R_{sh}H$ are the molecules of paraffin hydrocarbons. Each of reactions (I)–(IV) includes several elementary processes involving molecules and radicals of different structures. Step (III) is rate-limiting chain propagation. The product composition is determined by chain propagation reactions.
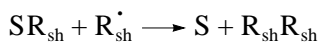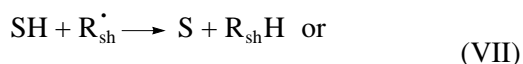
In the presence of catalysts (except for the gas-phase thermal reactions), the following processes occur on the surface [5, 6]:

$$S + RH \longrightarrow SH + R^• \ \text{ or } \ S + R_{sh}R \longrightarrow SR_{sh} + R^• \quad (V)$$

(heterogeneous initiation),

$$SR_{sh} \longrightarrow S + R_{sh}^{\cdot} \qquad (VI)$$

(dissociation),

$$SH + R_{sh}^{\cdot} \longrightarrow S + R_{sh}H \quad or$$
$$\qquad\qquad\qquad\qquad\qquad\qquad (VII)$$
$$SR_{sh} + R_{sh}^{\cdot} \longrightarrow S + R_{sh}R_{sh}$$

(regeneration of active sites), and

$$S + R_{sh}^{\cdot} \longrightarrow SR_{sh} \qquad (VIII)$$

(chain termination).

Here, S represents a generalized surface active site containing an unpaired electron. This can be a radical anion of the $O^{\overset{\cdot}{-}}$ type or a transition metal ion, a hole center, etc.

Reaction (V) is the heterogeneous initiation of a chain process. It would be completed immediately because of the consumption of active sites in reactions (V) and (VIII) if the regeneration of active sites S (VII) did not occur. In fact, the sequence of reactions (V), (VII), (V), (VII), … (heterogeneous initiation–regeneration) is heterogeneous chain propagation. Therefore, both homogeneous (II), (III), (II), (III), … and heterogeneous chain propagations take place in the presence of catalysts. It is impossible to separate the homogeneous and heterogeneous components because the chain can propagate via random pathways including both homogeneous and heterogeneous reactions, for example, (V), (II), (III), (II), (VII), (V), (VII), …, (VIII) or (II), (VII), (V), (III), (II), (VII), …, (IV).

The steady-state concentrations of active sites [S] and $[R_{sh}^{\cdot}]$ are related to and dependent on each other. The process rate is determined by the overall concentration of the free valence per unit reaction volume. In this case, the free valence partially belongs to the gas phase (radicals) and partially to the surface (active sites S).

The chain length during the thermal pyrolysis of hydrocarbons is of several units, and the rates of chain initiation and propagation are comparable. Therefore, the rate of hydrocarbon consumption under thermal conditions is the sum of the rates of homogeneous chain initiation and propagation: $w_t = w_1 + w_3'$. During catalytic pyrolysis, the rate of hydrocarbon consumption is $w_S = w_1 + w_3 + w_5$. The w_5 term in this equation can be substituted with w_7 if the heterogeneous chain propagation (in the sequence of reactions (V), (VII), (V), …) is limited by w_5 rather than by w_7. Taking into account that the catalyst affects the radical concentration in the gas phase, it can also influence the rate of homogeneous chain propagation w_3' may differ from w_3. Assuming that $[S]_0$ is the initial concentration of the surface active sites, the concentrations of the homogeneous $R_{sh}^{\cdot}$ and

heterogeneous S active sites are described by the following equations [6–8]:

$$[S] = (k_4[R_{sh}^{\cdot}]^2 \qquad\qquad (1)$$
$$+ k_7[S]_0[R_{sh}^{\cdot}] - w_1)/(k_5[RH] + k_7[R_{sh}^{\cdot}]),$$

$$w_1 + w_6 = [R_{sh}^{\cdot}]^2 + (k_4[R_{sh}^{\cdot}]^2 + k_7[S_0][R_{sh}^{\cdot}] - w_1) \qquad (2)$$
$$\times k_8[R_{sh}^{\cdot}]/(k_5[RH] + k_7[R_{sh}^{\cdot}]).$$

Using these equations, one can estimate the influence of the surface on a radical-chain process [6]. With the estimated steady-state concentrations of $R_{sh}^{\cdot}$ and S, one can assess the rates of all heterogeneous and homogeneous reactions, as well as the rate of a catalytic process w_S as a whole. For example, the rate constants for all elementary reactions of n-butane pyrolysis under thermal conditions were determined. As can be seen from the above kinetic scheme, the $R_{sh}^{\cdot}$ and S concentrations depend on the reactivity of the surface active sites S, which, in turn, is determined by the $E_{S–R}$ bond energies. Let us consider an energetically uniform surface with the active sites of the same reactivity. Then, the enthalpies of reactions (V) and (VII) can be estimated from the given $E_{S–R}$ values, and their activation energies and rate constants can be evaluated using the Polanyi–Semenov rule. Finally, by solving Eqs. (2) and (1), we can estimate the ratio of the rate of catalytic pyrolysis and thermal pyrolysis and thus assess the contribution of the catalyst to a radical-chain process [6].

Therefore, the rate of hydrocarbon pyrolysis with a catalyst is determined by the catalyst properties (the $E_{S–R}$ values, the initial concentration of surface active sites $[S]_0$, and the steady-state concentration of the interdependent active sites S and $R_{sh}^{\cdot}$). Henceforth, for the sake of simplicity, we will write [R] instead of $[R_{sh}^{\cdot}]$. Note that the catalyst affects the steady-state concentration [R] and causes its deviations from the thermodynamic-equilibrium value and from the steady-state value established during thermal pyrolysis under similar conditions (without a catalyst). Let us discuss this problem in more detail.

Most petrochemical processes are equilibrium, whereas the yield of the desired products in the thermal pyrolysis of hydrocarbons under conditions allowed by thermodynamics is controlled by kinetics. This is due to the high reactivity of radicals (consumed in both chain propagation and recombination), which determines the product distribution. When analyzing a radical-chain process, one should distinguish between the thermodynamic-equilibrium concentration of radicals (determined by thermodynamics) and the steady-state concentration (determined by the kinetic scheme of a radical-chain process). For example, during the thermal pyrolysis of ethane, the steady-state concentration of

methyl radicals is lower than their thermodynamic-equilibrium value, whereas the steady-state concentration of ethyl radicals is higher than their thermodynamic-equilibrium value [12]. For n-butane at 1000 K, the calculated thermodynamic-equilibrium constants $\log K_{eq}$ are –10 and –8.4 for methyl and ethyl radicals, respectively. The steady-state concentration of radicals calculated using the kinetic scheme of the thermal pyrolysis of n-butane under the same conditions $[R]_t = 4.5 \times 10^{-10}$ mol/cm^3. Therefore, the steady-state concentration of methyl radicals is higher than their thermodynamic-equilibrium value, whereas the steady-state concentration of the ethyl radicals is lower than their thermodynamic-equilibrium value. The existence of the overequilibrium concentration of at least one main radical is a typical feature of chain reactions, which ensures their occurrence and explains why a radical-chain process should be considered as a nonequilibrium one.

The catalysts for radical-chain processes (as well as the catalysts for any other chemical process) have no effect on the thermodynamic equilibrium of the formation of the pyrolysis products: ethylene, propylene, and other α-olefins. However, the catalyst affects the steady-state concentration of radical chain-carriers of the process and, as a consequence, the rate of the whole process, because the rate of the process in the presence of a catalyst is determined by the overall concentration of the free valence (R and S). The radical concentration during the reaction (the typical contact times during hydrocarbon pyrolysis $\tau = 1$–1.2 s) always attains its steady-state value both with and without a catalyst. In the presence of a catalyst, this value can be either higher or much lower than the thermodynamic-equilibrium concentrations of R. In the latter case, the process rate increases due to the high steady-state concentration of active sites S [7]. Therefore, it is better to compare the steady-state concentration of radicals for the catalytic radical-chain processes with their steady-state concentration established during thermal pyrolysis without a catalyst under similar conditions (temperature and pressure) rather than with their thermodynamic-equilibrium concentration. This can also be explained by the fact that the contribution of the catalyst is judged based on the comparison of the rates of the catalytic and thermal pyrolysis. The steady-state concentration of radicals during thermal pyrolysis $[R]_t$ will be referred to as "equilibrium" in quotation marks to distinguish it from the thermodynamic-equilibrium concentration without quotation marks.

Theoretical analysis of the phenomenological model [6, 7] suggests that there are four types of effects of a surface on a radical-chain process depending on the E_{S-R} values and the initial concentrations of surface active sites $[S]_0$: inhibiting, neutral, and accelerating either the heterogeneous or homogeneous component of the process. If the E_{S-R} values are comparable to the bond energies in the molecules subjected to pyrolysis (ranging within 300–400 kJ/mol), the surface catalyzes the process, and $w_S/w_t > 1$. The existence of four types of surface effects on radical-chain processes was experimentally confirmed in [11, 13–17].

The acceleration of the heterogeneous component is observed when the steady-state concentration of hydrocarbon radicals in the presence of a catalyst is below the "equilibrium" value $[R] < [R]_t$ [7, 16]. The process rate is determined by heterogeneous propagation (V), $w_5 \gg w_1$ and reaction $w_S = w_5$. For such catalysts, the main regularities of heterogeneous catalysis are valid.

Let us consider the fourth type of catalyst effect, the acceleration of the homogeneous component of the process rate. This acceleration is observed when the catalyst favors the formation of the overequilibrium concentration of radicals in the gas phase, and the catalytic contribution is due to homogeneous reactions in the gas phase: $[R] > [R]_t$, $w_3 > w_5$, and $w_S = w_3$ [7].

To elucidate the mechanism of the generation of the overequilibrium concentration of radicals, let us compare the main parameters of the thermal and catalytic pyrolysis for the acceleration of the homogeneous component. To illustrate, we used the phenomenological model to calculate the characteristic parameters of the thermal and catalytic pyrolysis of n-butane at 980 K and $E = 320$ kJ/mol, $[S]_0 = 2 \times 10^{-8}$ mol/ml. The calculation results are given in the table. Under these conditions, the step with w_7, $w_7 \ll w_5$, is rate-limiting for heterogeneous chain propagation. The rate of homogeneous initiation w_1 is much higher than the rate of heterogeneous initiation equal to w_7. However, it is the heterogeneous chain propagation that ensures the generation of additional radicals. An increase in the R concentration in the process including (V), (VII), (V), (II), (III), … is caused by the high steady-state concentration of active sites S involved in chain propagation (see table) and, hence, is due to kinetics. Therefore, the mechanism of the formation of overequilibrium radicals in our case differs from the mechanism of radical generation under irradiation when the rate of radical formation increases.

If active site S is considered as a point, then a sphere containing overequilibrium radicals in the gas phase surrounds it. If the active site is located on the surface, a hemisphere containing overequilibrium radicals is formed over it.

The space over the surface active site of a catalyst of a radical-chain process containing the overequilibrium concentration of radicals (as compared to thermal pyrolysis under similar conditions) is referred to as the catalysis sphere.[1] The catalysis sphere is typical only of radical-chain processes and catalysts accelerating the homogeneous component of a radical-chain process.

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[1] The notion of the catalysis sphere refers to any configuration of the space containing overequilibrium radicals. For example, the configuration depends on the location of an active site S. For the active sites located at the face, edge, or top of the crystal, the catalysis sphere configurations are different.

This term reflects the mechanism of the catalytic contribution of the sphere to the overall rate of the process and indicates that ordinary thermal pyrolysis occurs beyond this sphere. Catalysis is observed only within this sphere [8–11].

The catalyst surface contains a certain number of active sites S each generating a catalysis sphere. These catalysis spheres on and above the surface merge and form a continuous spatial (gas-phase) zone with a high radical concentration. The topography of merged spheres reflects the location of active sites on the surface. The radical catalysis occurs precisely within this zone packed with the spheres.

The catalysis sphere has a definite size and a complex structure. The size of the catalysis sphere, normal to the plane surface of a catalyst, determines the size of the zone of action of radical catalysis and is determined by the radii of the hemispheres containing the overequilibrium concentration of radicals. The size of the catalysis sphere should be taken into account in the technological design of a radical-chain process to ensure the best ratio of the catalyst surface to the free volume within which the sphere is formed.

Let us consider a plane catalyst surface (for example, the wall of a rectangular channel), over which the catalysis sphere is formed. The chain process over an active site S, developing normally to the surface, can be described by a classical equation:

$$D\partial^2[R]/\partial x^2 - k_4[R]^2 + w_1 = \partial[R]/\partial t, \qquad (3)$$

where the first term determines changes in the concentration of radicals during their diffusion from the catalyst surface ($x = 0$) to the gas phase over the distance x, the second term is the rate of the quadratic decay of radicals in the bulk of the gas phase, the third term is the rate of the thermal generation of radicals w_1, D is the diffusion coefficient, and k_4 is the rate constant of the homogeneous quadratic decay of radicals (reaction (IV)).

Fundamental studies of the surface effect on a radical-chain process usually considered the linear decay of radicals on the surface: radicals are thermally generated in the bulk and decay on the surface. The radical distribution near the surface is described by a hyperbolic function [18]. In this case, we have quite the opposite situation. Radicals are generated on the surface with parameters determined by the catalyst properties and the reaction conditions and are consumed by the quadratic law as they move away from the surface. We set the distance r, at which the radical concentration attains a value of $0.1([R]_0 - [R]_t)$, to be equal to the radius of
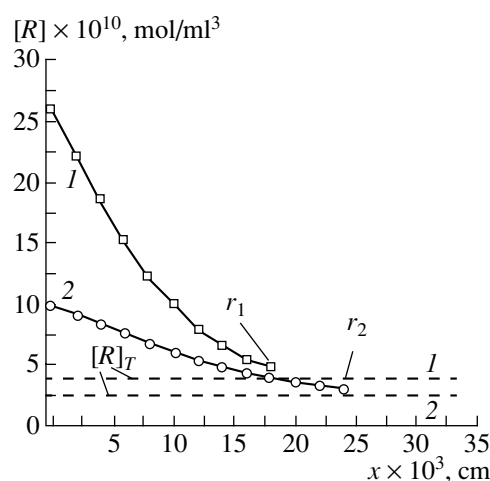
$[R] \times 10^{10}$, mol/ml^3

Radical distribution in the sphere: (*1*) $T = 1000$ K, $E = 300$ kJ/mol, $[S]_0 = 10^{-7}$ mol/ml, $[R]_0 = 2.6 \times 10^{-9}$ mol/ml, $[R]_t = 3.9 \times 10^{-10}$ mol/ml, and $r_1 = 1.8 \times 10^{-2}$ cm; (*2*) $T = 980$ K, $E = 320$ kJ/mol, $[S]_0 = 2 \times 10^{-7}$ mol/ml, $[R]_0 = 1 \times 10^{-9}$ mol/ml, $[R]_t = 2.5 \times 10^{-10}$ mol/ml, and $r_2 = 2.4 \times 10^{-2}$ cm.

the catalysis sphere. This radius of the sphere indicates that the distance between the walls of the channel of the catalyst block, where a radical-chain process occurs, should be less than $2r$. In this region, radical catalysis occurs. If the distance is more than $2r$, the reaction zone is used inefficiently because a region appears between the zones of radical catalysis where only thermal pyrolysis takes place.

When solving Eq. (3), we assume that the steady-state concentration of radicals $[R]_0$ is immediately established on the surface and that $[R]_0 = 10^{-9}$ at $x = 0$ and $[R]_t = 2.5 \times 10^{-10}$ mol/ml at $x = \infty$ (see table). The calculations were performed for the ethyl radical, $D = 0.65$ cm^2/s. At the initial moment $t = 0$, the first integration of Eq. (3) gives $(d[R]/dx)^2 = 2k_4 [R]^3/3D - 2w_1[R]/D + C$ (4). From the boundary conditions $d[R]/dx = 0$ at $x = \infty$ and $[R] = [R]_t$, we determine the integration constant C. Upon substituting $[R] = 10^{-9}$ mol/ml into Eq. (4) at $x = 0$, we obtain that $d[R]/dx = 6.578 \times 10^{-8}$. Using the gradient of the concentration of R at $t = 0$ and $x = 0$, we solve Eq. (3) by the method of finite differences. The curves calculated for the above conditions (see table) and for the conditions ensuring the higher overequilibrium concentration of radicals are presented in the figure. The relevant equilibrium concentrations of radicals are marked with dotted lines.

Main parameters of the thermal and catalytic pyrolysis of *n*-butane at 980 K

Reaction	[S], mol/ml	[R], mol/ml	w_1, mol ml^{-1} s^{-1}	w_5, mol ml^{-1} s^{-1}	w_7, mol ml^{-1} s^{-1}	w_3, mol ml^{-1} s^{-1}
Thermal pyrolysis	–	2.5×10^{-10}	2.5×10^{-6}	–	–	4.5×10^{-6}
Catalytic pyrolysis	1.6×10^{-8}	1.0×10^{-9}	2.5×10^{-6}	3.6×10^{-5}	6.0×10^{-8}	1.8×10^{-5}

The above data suggest a certain radical distribution within the sphere, which allows one to choose the appropriate radius of the catalysis sphere r. With an increase in the radical concentration, the sphere contracts in the direction of the surface. For example, $r = 1.8 \times 10^{-2}$ cm at 1000 K and $E = 300$ kJ/mol. This is due to the fact that the higher the radical concentration in the sphere, the more significant is the contribution of quadratic radical decay. For a decrease in the radical concentration, we have the opposite situation when the r value increases to 2.4×10^{-2} cm. However, the contribution of such a "dilute" sphere is insignificant. A real catalyst has a number of active sites S with different E values. We set $r = 2 \times 10^{-2}$ cm to be the average radius of the catalysis sphere during the catalytic pyrolysis of n-butane. The steady state in this sphere is established during $t = 3 \times 10^{-4}$ s. The distance between the opposite walls of catalyst channels for n-butane pyrolysis should be shorter than 4×10^{-2} cm. Therefore, one can set the requirements to the technological design of radical-chain processes using the radius of the catalysis sphere.

The radical distribution within the local catalysis sphere is presented in the figure. The catalysis spheres can overlap depending on the location of active sites S on the surface. Then, in each section of a separate catalysis sphere parallel to the catalyst surface at a distance Δx from the latter, there should be a distribution of overequilibrium radicals that continuously changes within the concentration range from $\sim 2[R]_0$ to $0.1\ ([R]_0 - [R]_t)$. Taking into account that the structure of the zone of radical catalysis is determined by the combination of incorporated catalysis spheres, the radical distribution within this space zone also has a complex dynamic nature that depends on both the activity of sites S and the degree of sphere overlap. The highest radical concentration in the catalysis sphere is observed right above an active site (see figure). When overequilibrium radicals move away from the site and diffuse in different directions, they participate in chain propagation and recombine (reaction (IV)). Therefore, the concentration of radicals decreases as they move away from a site S. The optimal steady-state concentration [S] should exist that determines the degree of the overlap of catalysis spheres. An insignificant overlap is preferable because it favors an increase in the concentration of radical carriers of the process. A stronger overlap is undesirable because an abrupt increase in the radical concentration in this case causes the same increase in the yield of radical recombination products, light paraffin hydrocarbons. As a result, the selectivity with respect to the desired products, α-olefins, will decrease.

The determination of the permissible degrees of overlap of the catalysis spheres for a particular radical-chain process is a separate theoretical and experimental problem. It is important that the sphere radius is a parameter that one can use to estimate the required optimal concentration of surface active sites S and the best density of the catalysis sphere packages.

To conclude, we note that the concept of the catalysis sphere considered for hydrocarbon pyrolysis is also applicable to other radical-chain processes, for example, dichloroethane pyrolysis [9]. The catalysis sphere can be formed in any catalytic process where the reaction is transformed from the catalyst surface to the gas phase. Simple experiments were performed that confirmed the formation of such a sphere [10, 11, 13–16]. The catalysis sphere concept not only extends the theory of catalysis by determining the zones of radical catalysis, but also forms a practical basis for the development of catalysts for radical-chain processes and their technological design.

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