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Physical Chemistry

Homogeneous Inhibition of Flame Propagation

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ABSTRACT. **The present paper studies the problem of modern fire-fighting modeling for inhibition of laminar flame by the particles of inorganic salts. The main goal of the work is to find out whether the inhibition stages can efficiently compete with the most important chemical processes proceeding in the flame (including the branching of the reaction chains). The inhibition of methane combustion, the simplest hydrocarbon, by the particles of sodium chloride of various size (their diameters comprised 5µm, 10µm and 20µm) was selected as the model process. For determination of the degree of heating and evaporation of solid particles in the flame zone the corresponding differential and integral equations were written. Their solution was carried out by numerical methods. The modeling showed that at flame extinguishing by small-size particles (*do* < 10µm) the homogeneous inhibition may efficiently compete with important gas-phase reactions in the moderate and high-temperature regions of the flame (T > 500 K). At flame extinguishing by the coarse-size particles (*do* > 20µm) much attention must be also given to the heterogeneous inhibition in the low-temperature region of the flame.** *© 2018 Bull. Georg. Natl. Acad. Sci.*

Key words: fire-fighting., fire extinguishing powders, flame inhibition, mathematical modeling

The study of the detailed mechanism of the effect of inhibiting additives on the combustion processes is one of the central problems of modern physical chemistry. Such investigations allow to reveal the internal regularities of combustion processes [1]. From this viewpoint the study of the inhibition of chemical reactions, developed in the combustion zone, and their modeling is of significant interest for further development of the combustion theory [2,3]. Along with it, these problems are directly associated with fire-fighting and prevention of inflammation of the combustible mixtures [4].

In the last few decades the special fire-fighting powders, prepared on the basis of the natural mineral resources and inorganic salts, are successfully used in fire-fighting practice. They are characterized by low toxicity, high activity and universal action [4-6]. Along with it the detailed mechanism isn’t adequately studied up to the present [3,5, 7-9].

Nowadays it is considered that at the inhibition of laminar flame by small-size particles (diameter < 10μm) of the powders of inorganic salts the gas-phase interaction of the active centers with the molecules, formed at evaporation of the particles in the flame zone, is of particular attention. The main goal of present paper is to elucidate of the problem: whether the inhibition stages efficiently compete with the most important chemical processes in the flame, in particular, with the branching of reaction chains.

The inhibition of the combustion of methane, the simplest hydrocarbon, was selected as the modeling process (the kinetic mechanism of the high-temperature oxidation of CH_4 is well-known at present). In accordance with the existing conceptions [8-10] the most important stages at methane oxidation present the “total” branching of the reaction chains (I) as well as the stage of formaldehyde formation (II):

$H + O_2 \rightarrow OH + O$ (I)

$CH_3 + O_2 \rightarrow H_2CO + OH$ (II)

As it is seen, the mentioned stages take place by the participation of active centers of the reaction, H atoms and CH_3 radicals. On this basis the flame inhibition by the powder additives implies the additional breakage of the reaction chains including the mentioned centers.

In accordance with [8], the homogenous inhibition of the flame by solid particles of inorganic salts most likely involves the following stages: a) evaporation of particles in the flame zone; b) the rapid formation of the molecules of metal hydroxides *(MeOH)* in gaseous phase; c) the interaction of formed hydroxides with the leading active centers of the reaction causing the reduction of combustion rate.

Let us consider the temperature profile of heating zone of the laminar kinetic flame. In accordance with the “heat” theory of the flame propagation [7, 9], in the mentioned zone the increase of temperature (T) of gaseous phase can be described by exponential function:

$$T = a + be^{x/l}, \qquad (1)$$

wherein

$$l = \frac{\bar{\lambda}}{c_p \rho_0 v_0}. \qquad (2)$$

In this expressions x represents the coordinate taken along the normal to the flame front, l - arbitrary thickness of the heating zone, $\bar{\lambda}$ -average coefficient of the mixture heat conduction, c_p - heat capacity of the gas, v_0 -fundamental rate of the combustion, ρ_0- density of initial air-fuel mixture. Coefficients a and b present the empirical values.

The degree of the exaporation of spherical solid particles- β(x), together with the other physical-chemical factors, depends on the particles temperature (θ) and on the corresponding diameter (d_s). At the displacement of the particles in the flame the variation of the mentioned parameters may be roughly described by the following equations [8]:

$$\frac{d\theta}{dx} = 12\,\frac{\lambda\,(T-\theta)}{V\,c_s\,\rho_s\,{d_s}^2}\,, \qquad (3)$$

$$d_s = d_0 - \frac{8M}{V}\int_0^x \frac{\lambda\,(T-\theta)}{\rho_s\,L}\,dx\,, \qquad (4)$$

$$\beta\,(x) = 1 - \left(\frac{d_s}{d_0}\right)^3. \qquad (5)$$

In these equations λ presents the coefficient of the gas heat conduction, V- the rate of mutual displacement of the solid particle and flame front, C_s and ρ_s represent specific heat capacity and density of the particle, respectively, M - molar mass of the molecule, L- molar heat of the particle evaporation, d_0- initial diameter of solid particle.

For modeling the following system was selected: propagation of laminar flame inhibited by the solid spherical particles of NaCl in the initial mixture of the following composition: 10% CH_4 and 90% air. Total pressure of the mixture - 1 atmosphere, initial temperature-300K (it should be noted that earlier we carried out the corresponding experiment) [10]. In the given case v_0 =0.45m · s^{-1} and V=3m · s^{-1}.. Initial diameters of the solid particles comprised 5μm, 10μm and 20μm and their content in gaseous mixture 0.1 kg/m^3 (such concentration of the particles provided considerable reduction of the flame propagation rate in methane-air mixture and decay of the flame intensity). The physical characteristics of the system under consideration and their temperature dependences were calculated by the well-known data of the handbooks [11, 12]. At modeling the melting of the solid particles in the flame zone at their displacement was also taken into account. In the course of the solution of the equations (3) and (4) the numerical methods of differentiation and integration were used [13]. Obtained results are presented in Fig.1.

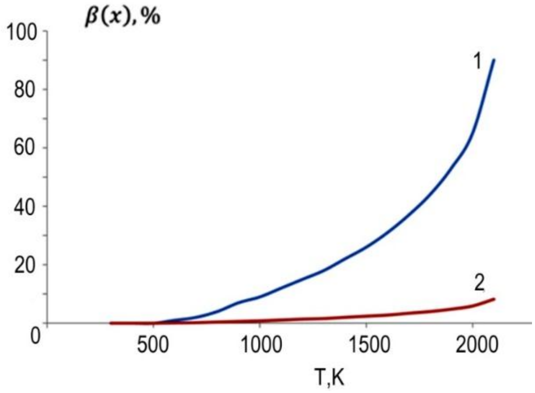

Fig. 1. Dependence of the evaporarion degree of particles on temperature in flame zone: (1) d_0 = 5 µm ; (2) d_0 = 10 µm .

The theoretical analysis show that the following stages are the most efficient way of gas-phase inhibition:

H + NaOH → Na + H_2O (III)

CH_3 + NaOH → Na + CH_3OH (IV)

These processes are exothermic and are to be characterized by low activation energy (E) in accordance with Semenov's rule [14].

For quantitative description of the flame inhibition in the previous work [15] we introduced coefficient α which was determined as the ratio between the decay rate of the active center and the rate of the most important stage by participation of the mentioned center. The following equations may be written:

$$\alpha_1 = \frac{\omega(III)}{\omega(I)} = \frac{k\,(III)[NaOH]}{k\,(I)[O_2]}\,, \qquad (6)$$

$$\alpha_2 = \frac{\omega(IV)}{\omega(II)} = \frac{k\,(IV)[NaOH]}{k\,(II)[O_2]}\,. \qquad (7)$$

Here, ω(i) and $k(\,i\,)$ present the rate of i-stage and the corresponding rate constant, respectively. In the square brackets the molar concentrations of the molecular components are written. Proceeding from the aforesaid, the conditions of the efficient inhibition can be written in the following manner:

$$\lg \alpha_1 \geq 0\,, \lg \alpha_2 \geq 0\,. \qquad (8)$$

For calculation of the values $k(I)$ and $k(II)$ the well-known handbook data were used [16]. To describe the temperature dependences of the constants $k(III)$ and $k(IV)$ the Arrhenius equation was used:

$$\text{k (III)} = \text{A(III)}\; e^{-\,1350/RT}\,, \qquad (9)$$

$$\text{k (IV)} = \text{A(IV)}\; e^{-\,8250/RT}. \qquad (10)$$

In this expressions A(i) present the pre-exponential factors for the rate constants. Because of the fact that the exact values of the A(III) and A(IV) are not known, various probable numerical values were provided at the use of the expressions (9) and (10).

For description of temperature dependence of the concentration of molecular oxygen in the flame zone the principle of "similarity of concentration and temperature fields" was used [7, 9]. As to [NaOH] value, for its calculation the content of the powder particles in the flame (see above) and the data of the degree of their evaporation (from Fig.1) were used.

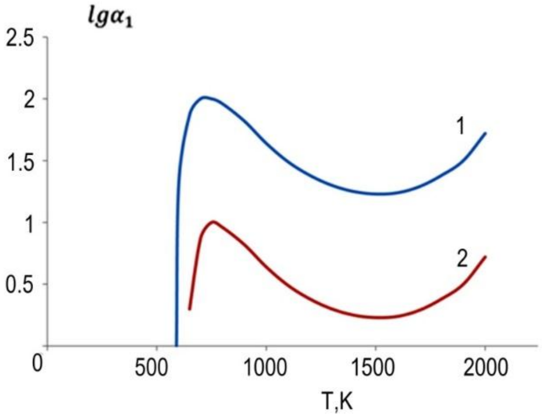

Fig. 2. Curve of the α_1 coefficient variation (d_0 = 5 µm): *A(III)* = $10^{14}\,cm^3\;mol^{-1}\;s^{-1}$, *A(III)* = $10^{13}\;cm^3\;mol^{-1}\,s^{-1}$.

The results of the calculations are presented in Fig.2-4. As it is seen, the conditions of the efficient inhibition (8) are fulfilled for the moderate and high temperatures when T>500K. It is also evident, that the greater is the numerical value of A(III) and A(IV) the broader is the temperature interval of the efficient inhibition in the flame zone.

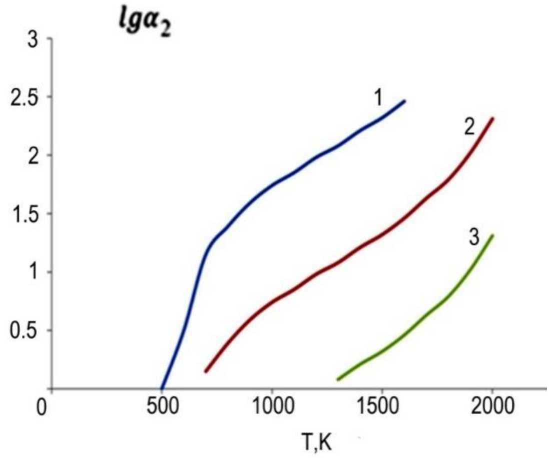

Fig. 3. A plot of $lg\ \alpha_2$ versus T (d_0 = 5 μm):

(1) $A(IV) = 10^{14}\ cm^3\ mol^{-1}\ s^{-1}$,
(2) $A(IV) = 10^{13}\ cm^3\ mol^{-1}\ s^{-1}$,
(3) $A(IV) = 10^{12}\ cm^3\ mol^{-1}\ s^{-1}$.

The calculations were also performed for the coarse-size particles when $do = 20$μm. It was found that in this case $\beta(x)$ is no more than 2%. This means that the content of the inhibitor, passed in gaseous phase, and respectively, the effect of the homogenous inhibition on the combustion processes is considerably low.

As the conclusion, the following can be said: at extinguishing of methane laminar flame by the small-size particles (do <10μm) the homogenous inhibition may efficiently compete with important gas-phase stages in the reaction zone in moderate- and high-temperature regions of the flame. At extinguishing the methane flame by the coarse-size particles (do>20μm) the role of the homogenous inhibition is negligible and in such conditions the heterogeneous inhibition in the low-temperature region attaches much importance.

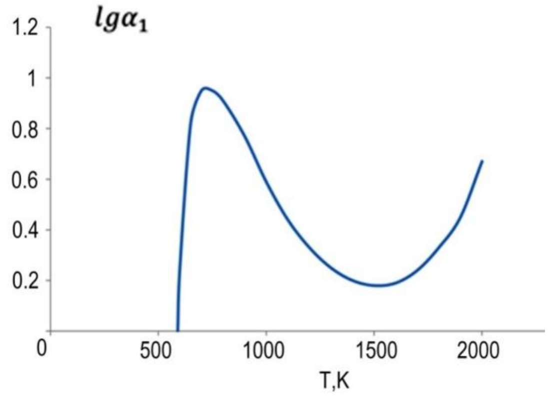

Fig. 4. Curve of the $lg\ \alpha_1$ variation (d_0 = 10 μm):
$A(III) = 10^{14}\ cm^3\ mol^{-1}\ s^{-1}$.

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ფიზიკური ქიმია

ალის გავრცელების ჰომოგენური ინჰიბირება

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ნაშრომში შესწავლილია თანამედროვე ხანძართქრობისათვის მნიშვნელოვანი საკითხი - არაორგანული მარილის ნაწილაკებით ლამინარული ალის ინჰიბირების მოდელირება. ნაშრომის ძირითად მიზანს შეადგენდა იმის გარკვევა, შეუძლიათ თუ არა ინჰიბირების სტადიებს ეფექტური კონკურენცია გაუწიონ ალის ზონაში მიმდინარე უმნიშვნელოვანეს ქიმიურ პროცესებს, მათ შორის, სარეაქციო ჯაჭვების განშტოებას. მოდელურ პროცესად შერჩეული იყო უმარტივესი ნახშირწყალბადის, მეთანის წვის ინჰიბირება ნატრიუმის ქლორიდის სხვადასხვა ზომის ნაწილაკებით (დიამეტრებით 5 მკმ, 10 მკმ და 20 მკმ). ალის ზონაში მყარ ნაწილაკთა გახურებისა და აქროლების ხარისხის განსაზღვრისათვის ჩაწერილ იქნა სათანადო დიფერენციალური და ინტეგრალური განტოლებები, რომელთა ამოხსნაც განხორციელდა რიცხვითი მეთოდებით. მოდელირებამ აჩვენა, რომ მცირე ზომის ნაწილაკებით ($d_0 < 10$ მკმ) ალის ჩაქრობისას ჰომოგენურ ინჰიბირებას შეუძლია ეფექტური კონკურენცია გაუწიოს მნიშვნელოვან აირადფაზურ რეაქციებს ალის ზომიერ და მაღალტემპერატურულ უბნებში ($T > 500$ K). მსხვილი ნაწილაკებით ($d_0 > 20$ მკმ) ალის ჩაქრობისას დიდი მნიშვნელობა უნდა მიენიჭოს აგრეთვე ჰეტეროგენულ ინჰიბირებას ალის დაბალტემპერატურულ უბანში.

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