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Influence of noble metals on thermoacoustic oscillations and boundaries of the region of negative temperature coefficient during combustion of *n*-pentane – air mixtures

Nikolai M. Rubtsov,*[a] Georgii I. Tsvetkov,[a] Victor I. Chernysh[a] and Kirill Ya. Troshin[b]

[a] *Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 495 962 8025; e-mail: nmrubtss@mail.ru*

[b] *N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation*

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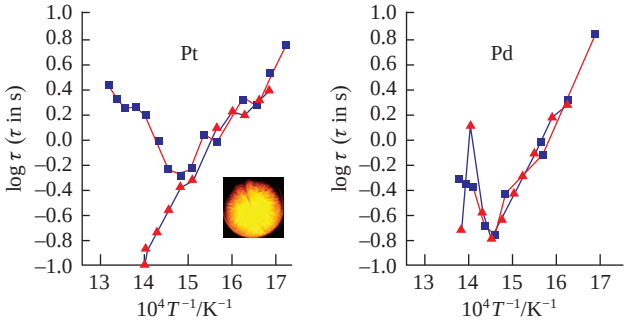
Using the combustion of *n*-pentane – air mixtures as an example, it was shown that thermoacoustic regimes of ignition disappear in the presence of a platinum surface, which generates catalytic centers propagating into the volume. Thus, the platinum catalyst eliminates a certain stage of kinetic mechanism, and the negative temperature coefficient phenomenon vanishes. In the presence of a palladium catalytic surface that does not generate catalytic centers propagating into the volume, the phenomenon of a negative temperature coefficient occurs.



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The study of hydrocarbon ignition is of obvious importance, but there is no complete clarity regarding the mysterious phenomena inherent in this process. These are stepwise ignition and a negative temperature coefficient (NTC) observed at fairly low temperatures. NTC is the increase in the delay time of thermal ignition (hereinafter referred to as autoignition) with reactor temperature growth in a certain temperature range. It causes undesirable phenomena in internal combustion engines.[1,2] There is no consensus on the detailed mechanisms of hydrocarbon oxidation in this temperature range, as well as on the understanding of the NTC phenomenon. In practical engine operating conditions, hydrocarbon fuels can be divided into two types according to ignition characteristics: fuels characterized by single-stage autoignition, such as aromatics and alcohols, and fuels characterized by two-stage autoignition, such as *n*-paraffins, unsaturated and cyclic hydrocarbons with an NTC region observed at < 850 K. When two-stage ignition occurs, first-stage ignition takes on a significant role, since second-stage ignition depends on the release of heat and intermediate species generated in the first stage. Furthermore, the NTC region of the total ignition delay covers exactly the temperature range that is relevant to engine knock and related combustion phenomena.[3,4] Because hydrocarbons with two-stage autoignition typically make up more than a half of practical fuels,[5] engine processes controlled by combustion kinetics, such as homogeneous charge compression ignition, would occur in two stages as well; the stage of low-temperature heat release is followed by the stage of high-temperature heat release. Note that fuels with two-stage ignition offer significant advantages in controlling combustion phasing and extending the operating range of homogeneous charge compression ignition.[6,7] Thus, it is essential to better understand the NTC phenomenon in order to develop new control strategies to save fuel and reduce pollutant emissions.

It should be noted that, according to published data,[8,9] autoignition in a shock tube and a rapid compression machine is of a kernel nature. Previously, we have shown[10] that the ignition of the *n*-pentane – air mixtures in a rapid mixture injection static reactor at 1 atm begins with the formation of a primary center at the most chemically active site on the surface. The center initiates the propagation of a hemispherical flame front with normal velocity corresponding to the wall temperature and gas composition. Therefore, the reaction never starts in the entire volume, especially if there is no active surface in this volume, *e.g.*, aerosols.[10]

Earlier, we conducted a series of experiments to determine whether the catalyst affects the ignition of hydrocarbons,[11] and obtained the following results. It turned out that only one kernel is formed on the Pt surface at temperatures in the NTC range, while at higher temperatures multiple kernels are observed. The pressure oscillograms upon ignition under the same conditions in the absence and presence of a catalytic surface showed that, without Pt, a cool flame ignition, accompanied with a small warming up, quickly transforms into hot. Ignition kernels develop rapidly, indicating the onset of hot ignition, while stepwise ignition and cool flames precede the stage of hot ignition. However, in different temperature regions, Pt surface influenced the ignition differently. In particular, at low temperature, the Pt surface had no appreciable effect on the ignition delay time, but in the temperature range in which NTC is usually observed, the presence of the Pt surface completely eliminated the NTC phenomenon.[11] Since ignition delay in this case occurred as if there was no difference between cool flame and hot ignition in the temperature range corresponding to the NTC, we concluded that the catalytic surface eliminates a certain stage of the kinetic mechanism (inhibition stage) after the emergence of the cool flame. This effect is very significant for elucidating the nature of the

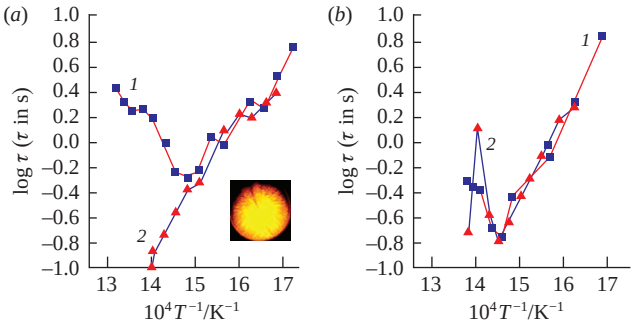

Figure 1 Typical temperature dependences of the ignition delay time τ (s) for a stoichiometric *n*-pentane–air mixture at an initial pressure of 3 atm in the (*1*) absence and (*2*) presence of (*a*) Pt and (*b*) Pd catalytic surfaces. The data in the absence of a catalyst surface were obtained in the reactor used for the catalyst experiments, in which the surface layer was scraped off mechanically. Inset: Frame of combustion of a mixture of 40% H_2 + 60% air at a reactor wall temperature of 316 °C with Pt wire placed in the stainless steel reactor.[13]

intermediate products of the reaction, which are probably responsible for the existence of the NTC phenomenon. However, it remains unclear how a Pt wire localized in a small volume has such a noticeable effect on the volume process.

The aim of this work is to establish the features of the influence of noble metals (Pt, Pd) on specific combustion modes in the region of NTC.

First, by direct measurements of the temperature[12] in the center of the reactor (10 cm in diameter and 10 cm in length) with thin 25 mm thermocouples at atmospheric pressure and a temperature of 800–980 K, it was shown that the time of warming up the gas mixture does not exceed 0.2 s, which much less than the time obtained using an equation that takes into account only conductive heat exchange. Figure 1(*a*) compares experimental data on the ignition delay times of a stoichiometric *n*-pentane–air mixture in the reactor in the absence and presence of a Pt catalytic surface. As can be seen from Figure 1(*a*), in the region of the positive temperature coefficient at lower temperatures, the Pt catalytic surface has almost no effect on the ignition delay time, *i.e.*, the process of ignition. However, in the region of the negative temperature coefficient, the role of the Pt catalytic surface, according to the literature data,[11] becomes very significant. In the presence of Pt wire, the ignition delay time only decreases with increasing temperature, and the NTC region is absent. To reproduce the data corresponding to the absence of Pt catalyst after experiments with Pt wire in the reactor, 0.5 mm thick inner surface layer of the reactor was scraped off mechanically.

Pressure oscillograms upon ignition under the same conditions in the absence and presence of Pt are presented in Figure 2(*a*),(*b*). Pt-catalyzed ignition is located along the surface of the wire, *i.e.*, it serves as an ignition source. Since the ignition delay time in this case behaves as if there is no difference between cool flame and hot ignition in the temperature region corresponding to the NTC according to published data,[11] it can be concluded that the Pt surface eliminates a certain stage of the ignition mechanism, probably the inhibition reaction, after occurrence of the cool flame.

As can be seen in Figure 2(*a*), in the absence of the Pt catalytic surface, hot ignition in the NTC region is accompanied by thermoacoustic oscillations, the maximum amplitude of which is attained around the middle of the NTC temperature region. The oscillation frequency is about 500 Hz, which roughly corresponds to the first mode of oscillations of a hollow vessel with dimensions close to the reactor used in this work.[14] However, in the presence of the Pt catalytic surface, oscillations are no longer observed [Figure 2(*b*)]. According to Lord Rayleigh's principle[15] for heat driven pressure oscillations, thermoacoustic instability is encouraged when the heat release fluctuates in phase with the pressure perturbation. Thus, in the presence of Pt, the heat release and pressure perturbation during combustion occur out of phase, which is consistent with the above statement that the Pt catalytic surface eliminates a certain stage of combustion after the occurrence of the cool flame. This stage can be, *e.g.*, the decomposition of the slow-reacting intermediate peroxide on the Pt surface to form a more reactive surface radical, for instance O and/or OH, which can be desorbed.

Such a mechanism was proposed earlier[16] for the decomposition of hydrogen peroxide over Pt. It results in changing the rate of heat release during hot ignition. The detailed mechanism of this stage of hydrocarbon oxidation obviously requires further consideration, since experimental data on the reactions of gaseous alkyl peroxides on the surface of platinum are very scarce to date. Seemingly, a thin Pt wire occupies a small volume and cannot influence the combustion process in a gas. It has long been known[17] that, at temperatures > 500 °C, molecules or clusters of both PtO_2 and platinum metal occur in the gas phase. Previously, we showed[13] that these particles enter the reactor volume by diffusion and convection [Figure 1 (*a*), inset] and act as catalytic centers on which ignition takes place during the propagation of the flame front. These are centers whose reactions strongly influence the combustion mechanism.

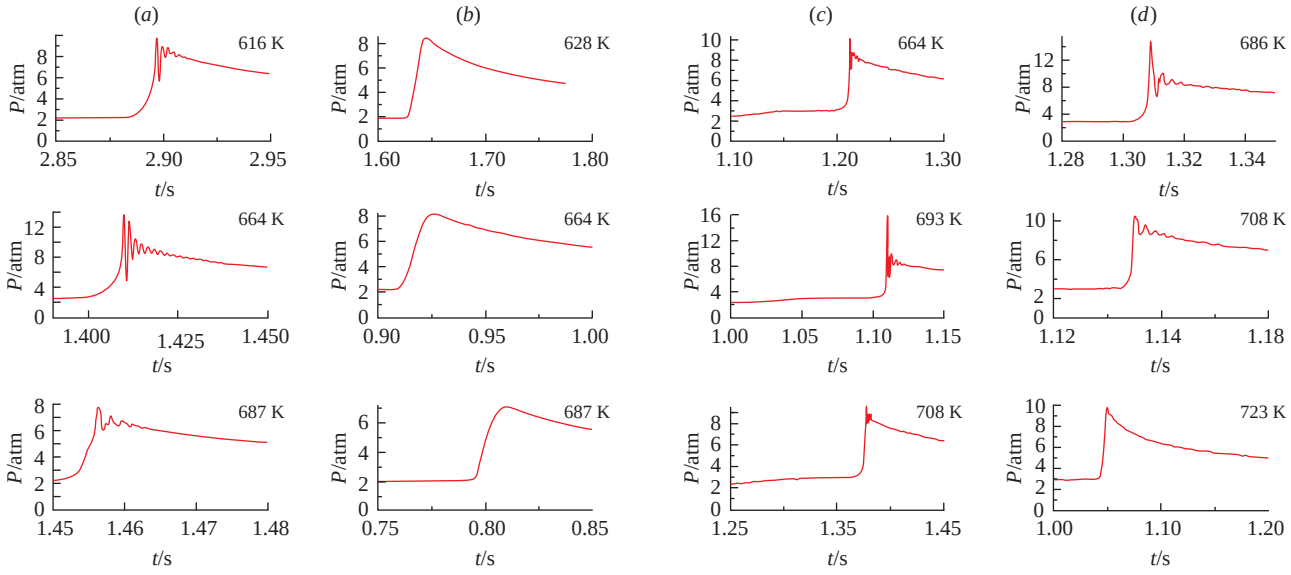

Figure 2 Oscillograms of pressure changes upon ignition of stoichiometric *n*-pentane–air mixtures at different temperatures in the NTC region (*a*) in the absence of a catalytic surface, (*b*) in the presence of Pt wire, (*c*) in the absence of a catalytic surface after preliminary scraping of the inner surface layer of the reactor and (*d*) in the presence of Pd wire.

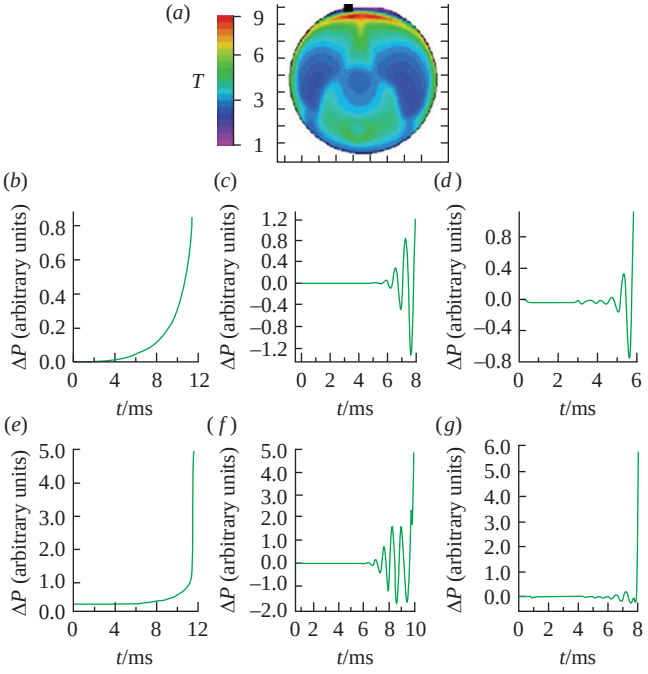

Figure 3 Results of numerical calculation of the system of compressible dimensionless reactive Navier–Stokes equations in the low Mach number approximation, which describes flame propagation in a two-dimensional area: (*a*) calculated temperature field; (*b*)–(*g*) kinetic pressure curves calculated at the point on the top of the reactor (indicated by a square) for given activation energies of two radical reactions (*b*)–(*d*) $\zeta = 4$, $\zeta_1 = 7.5$ or (*e*)–(*g*) $\zeta = 7.5$, $\zeta_1 = 4$ and initial dimensionless wall temperature (*b*),(*e*) $T = 3$, (*c*),(*f*) $T = 6$ and (*d*),(*g*) $T = 9$.

As can be seen in Figure 2(*b*), both in the region of the positive temperature coefficient and in the NTC region, the Pt catalytic surface has almost no effect on the ignition delay time, *i.e.*, ignition process. The result obtained agrees with the published data,[18] which show that, in the presence of Pd foil, no cellular structure of the flame front is observed upon ignition of $H_2–CH_4–$air mixtures, in contrast to the results obtained on the Pt surface. This is due to the greater stability of PdO compared to PtO_2, which is very unstable and decomposes at temperatures above 500 °C (*vide supra*). Figure 2(*c*),(*d*) displays pressure oscillograms for ignition under the same conditions in the absence and presence of the Pd catalytic surface. As can be noted, hot ignition both in the absence and in the presence of the Pd catalytic surface in the NTC region is accompanied by thermoacoustic oscillations, the maximum amplitude of which is reached in the middle of the NTC region. This is an additional indication that in the presence of a catalytic surface that does not noticeably react with oxygen at the temperature of the flame and does not generate catalytic centers propagating into the volume, the NTC phenomenon occurs. The regularities found must be taken into account in the numerical simulation of the NTC region: both oscillations and the NTC region must disappear after a certain reaction or a series of reaction stages is excluded from the mechanism. The stage must include a surface reaction of the active combustion intermediate on Pt surface, in which more active intermediates are formed from a low-activity intermediate.

We attempted to qualitatively illustrate the influence of the chemical mechanism and heat release on a simple example of a sequence of two chemical chain reactions by numerical modeling using the previously presented[19–21] system of compressible dimensionless reactive Navier–Stokes equations in the low Mach number approximation, which describes flame propagation in a two-dimensional area. Unlike the system of Navier–Stokes equations used in previous works,[19–21] here the combustion process was represented not by a simple Arrhenius equation, but by an elementary chain mechanism:

$$C \rightarrow 2n \quad (w_0),$$
$$n + C \rightarrow 2n + n_1 + \text{products} \quad (\beta_0,\ Q = \beta_1)$$

and

$$n_1 + C \rightarrow n + \text{products} \quad (\beta,\ Q = \beta_2),$$

where Q is the heat release in the stage, and all other parameters, except for the diffusion coefficients (*vide infra*), were the same as in the published work.[20] The chain initiation reaction w_0 can be neglected.[20] In this case, the simple Arrhenius equation, as in the mentioned work,[20] was replaced by the following equations:

$$\rho(C_t + \nu C_y + u C_x) = \Delta^2 C + w_0 - \beta_0 n W - \beta n_1 W_1, \quad (1)$$
$$\rho(n_t + \nu n_y + u n_x) = \Delta^2 n + w_0 + 2\beta_0 n W + \beta n_1 W_1, \quad (2)$$
$$\rho(n_{1t} + \nu n_{1y} + u n_{1x}) = \Delta^2 n + \beta_0 n W - \beta n_1 W_1, \quad (3)$$
$$W = C \exp(\zeta - \zeta/T), \quad (4)$$
$$W = C \exp(\zeta_1 - \zeta_1/T), \quad (5)$$

where β_0 and β are the kinetic coefficients proportional to the corresponding Damköhler numbers. The following parameter values were assumed to be $\zeta = 4$, $\zeta_1 = 7.5$, $\beta_0 = 0.1$, $\beta = 0.15$, $\beta_1 = 0.22$, $\beta_2 = 0.3$ and $T_t = T - T_0$, as well as diffusion coefficients $D_n = D_{n1} = 0.3$. The problem was solved by the finite element analysis using the FlexPDE 6.08 software package (PDE Solutions Inc., 1996–2008).[22]

The results of the calculation of thermoacoustic oscillations in the reaction set are shown in Figure 3. It is seen that at $T = 6$ the oscillations during combustion are most intense, and at $T = 3$ and $T = 9$ the oscillations are less intense; it qualitatively illustrates the experiment. As can also be seen from the figure, the mutual rearrangement of the values of the activation energies for two radical reactions leads to noticeable changes in the modes of thermoacoustic oscillations. Most likely, this is due to the fact that heat release and pressure perturbation for $\zeta = 4$, $\zeta_1 = 7.5$ during combustion are more out of phase than for $\zeta = 7.5$, $\zeta_1 = 4$ at the expense of changing the time dependences of heat release during combustion.

It should be noted that the analysis of the first chemical reaction with the exclusion of the second ($\beta = 0$), which is equivalent to its complete inhibition, does not lead to the effect. However, with an increase in the initial temperature, the intensity of thermoacoustic oscillations first increases and then decreases.

Therefore it is clear that a reliable microkinetic model must take into account the occurrence of thermoacoustic oscillations; the exclusion of a certain stage of the kinetic mechanism (probably of a superficial nature) should cause the disappearance of the NTC mode of the reaction.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.09.043.

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