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The phenomenon of negative temperature coefficient in palladium-initiated combustion of hydrogen–propane–air mixtures

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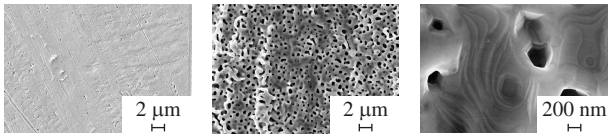
During the combustion of hydrogen (70–40%) + propane (30–60%) + air mixtures over palladium at a total pressure of 1–2 atm, Pd is consumed in the chemical etching reaction with active combustion intermediates. This behaviour of palladium limits its applicability in ignition devices.



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Studying the ignition of fuels, mainly hydrocarbons or hydrogen–hydrocarbon mixed fuels, is of obvious practical importance, however up to now, there is no complete clarity about the phenomena accompanying this process. The most poorly understood are stepwise ignition and a negative temperature coefficient (NTC), observed at considerably low temperature.[1] NTC is an increase in the ignition delay time with increasing temperature in a definite range. It causes undesirable phenomena in internal combustion engines.[2,3] There is no consensus on the detailed mechanism of hydrocarbon oxidation at temperatures below 600 °C, as well as on the nature of the NTC phenomenon. It was experimentally shown using a static reactor for rapid injection of the mixture that at temperatures < 660 K, the catalytic Pt surface does not significantly affect the ignition delay time of the stoichiometric *n*-pentane–air mixture. However, in the temperature range in which NTC is usually observed, the presence of a Pt surface excludes its occurrence.[1] The revealed feature seems to be the key to understanding the NTC phenomenon.

Noble metals have different effects on the flammability of hydrogen–hydrocarbon mixtures. It was shown that the ignition temperature of a mixture of 40% H_2 with air over the Pd metal (70 °C, 1 atm) is ~200 °C lower than that over the Pt surface (260 °C, 1 atm).[4,5] Besides, Pd ignites stoichiometric mixtures of (30–60% H_2 + 70–40% CH_4) + air (ϕ = 1),[†] while metallic Pt cannot ignite these mixtures up to 450 °C; hence, Pd is more effective than Pt. Although the cellular structure of the flame front was absent upon ignition with Pd, it was observed over the Pt surface. Thus, Pd seems to be more suitable for hydrogen recombinators in nuclear power plants because catalytic particles as ignition centers formed during the decomposition of volatile oxide cannot occur in the gas phase, unlike Pt catalysis.[1] The experimental value of the effective activation energy of the process is estimated as 3.5 ± 1 kcal mol^{-1} that is characteristic of a surface process. This indicates a noticeable role of the flameless 'dark' reaction in consumption of H_2 and O_2 over Pd observed directly at low pressures.[4]

It was found that the value of the 'upper' temperature limit of ignition over the surface of palladium at 1.75 atm, measured with a bottom-up approach (when the temperature increases from the state of no ignition), for the mixtures of (30% methane + 70% hydrogen) + air (ϕ = 0.9, T = 317 °C) and (30% propane + 70% hydrogen) + air (ϕ = 1, 106 °C) decreases after subsequent ignitions to the 'lower' ignition limit (when the temperature decreases from the state of autoignition), and amounts to 270 °C for the hydrogen–methane mixture and 32 °C for the hydrogen–propane mixture. The temperature limit of ignition returns to the initial 'upper' value after treating the reactor with oxygen or air, *i.e.*, a hysteresis effect occurs. Thus, the 'lower' limit of ignition corresponds to the reactor or Pd surface treated with ignitions, and the 'upper' one corresponds to the 'fresh' reactor, in which no ignitions occurred before.

As seen from the above, both noble metals hardly influence the NTC phenomenon and also give rise to the hysteresis effect during the combustion of hydrogen–hydrocarbon mixtures. These factors give good grounds to expect NTC phenomena in the low-temperature area of the hysteresis effect during the combustion of these gas mixtures.

In this work, the phenomenon of low-temperature NTC in the hysteresis area was detected and investigated by the example of combustion of (70–40% hydrogen + 30–60% propane) + air mixtures with ϕ = 1 over Pd at a total pressure of 1–2 atm. The dependencies of the ignition delay period (the so-called 'induction period') on time and the flammability limit on temperature were also examined over the Pd surface.

Time dependencies of the temperature of the Pd wire during the ignition of C_3H_8 + H_2 + air mixtures [Figures 1(*a*),(*b*)] correspond to successive temperature values below the 'upper' temperature limit of ignition, measured with a bottom-up approach by increasing the temperature from the state of no ignition. According to Figures 1(*a*),(*b*), ignition delay (induction) period τ first decreases with decreasing temperature, but then the τ value increases until the 'lower' temperature limit of ignition is reached (when the temperature decreases from the state of

[†] The equivalence ratio ϕ is a fraction of fuel in the mixture with air: $\phi H_2 + 0.5\,(O_2 + 3.76\,N_2)$.

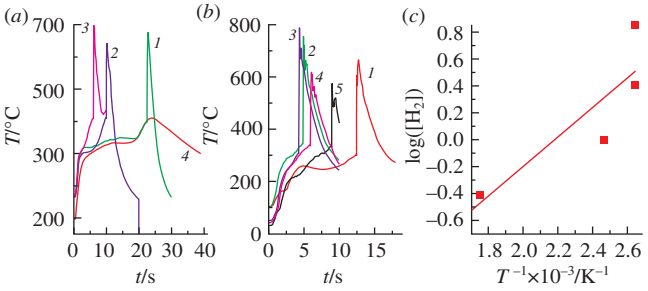

Figure 1 The change in the temperature of the Pd wire during the ignition of (*a*) 60% C_3H_8 + 40% H_2 + air mixture at an initial temperature of (*1*) 174, (*2*) 168, (*3*) 165 and (*4*) 98 °C and (*b*) 40% C_3H_8 + 60% H_2 + air mixture at an initial temperature of (*1*) 104, (*2*) 102, (*3*) 58, (*4*) 45 and (*5*) 38 °C. The total pressure was 1.75 atm. The ignition delay (induction period) τ can be seen in the figure. (*c*) Arrhenius plot of the experimental dependence of the H_2 fraction [H_2] at the 'upper' temperature limit of ignition and a total pressure of 1.75 atm.

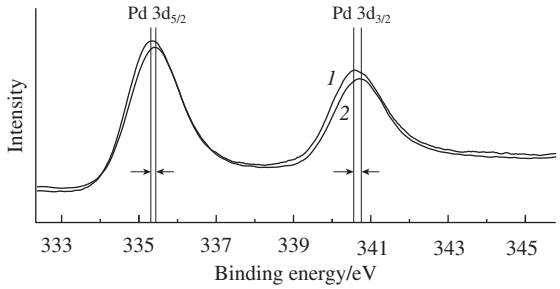

Figure 2 The Pd $3d_{5/2}$ and Pd $3d_{3/2}$ photoelectron spectra obtained from (*1*) initial Pd foil and (*2*) Pd foil treated with 70 ignitions of (30–60% H_2 + + 70–40% CH_4) + air mixture. Photon energy is 460 eV.

autoignition). Thus, the observed NTC phenomenon is somewhat similar to the one known in the literature.[1] In our case, the NTC phenomenon has an obvious explanation. It is caused by a change in the state of the Pd surface.

The dependence of the H_2 fraction at the 'upper' temperature limits of ignition (when the temperature increases from the state of no ignition) in the mixtures under investigation is presented in Figure 1(*c*) in Arrhenius coordinates similar to those in the published work.[5] As seen in Figure 1(*c*), the dependence can be approximated‡ by a straight line with a correlation coefficient of 0.978. The experimental value of the effective activation energy E of the process is 2.2 ± 1 kcal mol^{-1} that is characteristic of a surface process.[6,7] It should be noted that the value of the effective activation energy is close to that obtained from the dependence of the H_2 fraction in combustible mixtures on the temperature in Arrhenius coordinates for H_2–air and H_2–CH_4–air mixtures.[5] This also indicates that the detected NTC phenomenon is strongly related to the state of the Pd surface. In this regard, the Pd surface was examined before and after 50 ignitions using X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM).§

After the partial oxidation of methane over a Pd/Al_2O_3 catalyst,[8] XPS analysis revealed that peaks at lower binding energies (335 eV) are characteristic of metallic Pd, while those for PdO_x species appear slightly higher, at 336–337 eV. Due to air exposure during catalyst preparation and storage, Pd oxidizes to some degree in all samples heated to 500 K, but metallic Pd peaks at 335 eV are dominant at these lower temperatures. As the heat pretreatment temperature increases to 600 K and further to 650 K, the XPS signal characteristic of the PdO_x species at 336.0–336.2 eV becomes dominant for most particle sizes. In addition, metallic Pd (335 eV) also has a significant contribution to the X-ray photoelectron spectra, and the data show that a mixture of both Pd metal and Pd oxide is needed to continue the reaction after initial oxide formation. At temperatures above 700 K, the oxide species are reduced to metallic Pd. According to the above, the treated Pd sample contains more PdO than the initial one (Figure 2). PdO species arise due to gaseous oxidation and subsequently decompose again to Pd and O_2 at 900 °C in the heated gas.[9] It means that both Pd oxide and Pd metal in the form of molecules or clusters exist in the gaseous phase at temperatures above 900 °C. Notice that the maximum temperature of hydrogen–propane–air flame reaches 1600 °C under our conditions.

The SEM results indicate that the initial sample has a surface with rolling traces [Figure 3(*a*)]. In the sample treated with ignitions, defects develop in the form of volcanic holes [Figure 3(*b*)], reaching a depth of 1 μm. These defects are focused on the etching patterns [Figure 3(*c*)]. Obviously, the etching agents are the active intermediates in the oxidation of H_2 and CH_4.

The etching process can be easily vizualized using high-speed colour video (Figure 4). According to Figure 4, the orange particle flow moves upward simultaneously with the propagating flame front. The fact that the particles are rising indicates that they are hot. From the sequence of frames, it is clear that these particles occur close to the surface of palladium metal. From this observation, it can be concluded that ultradispersed PdO particles arise during the oxidation of the Pd surface and then partially decompose to Pd and O_2 at the temperature of the flame products. It means that the catalyst (Pd) is consumed in the chemical etching reaction, most likely with active flame intermediates. This feature should limit the use of palladium as a flame source in stationary ignition devices.

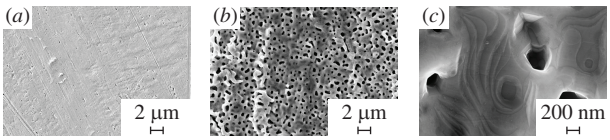

Figure 3 SEM images of the surface of (*a*) initial Pd foil and (*b*,*c*) treated Pd foil.

‡ The data were processed using the Statistica 9 software package (Statsoft).

§ The experiments were performed with gas mixtures of (70–40% hydrogen + 30–60% propane) + air (ϕ = 1) over Pd at a total pressure of 1–2 atm. A heated cylindrical stainless steel reactor with a length of 25 cm and a diameter of 14 cm, equipped with removable covers and an optical sapphire window in one of them, was used in the experiments.[6] The accuracy of the temperature measurement was 0.3 K. Registration of ignition and flame propagation was carried out using a colour high-speed Casio Exilim F1 Pro camera (frame rate 600 s^{-1}). The video file was stored in the computer memory, and its time-lapse processing was performed.[1] The evacuated and heated reactor was quickly filled with a gas mixture from the high-pressure buffer volume to the required pressure. The ignition limit was determined as the mean of two temperatures at a given pressure, *e.g.*, for a bottom-up approach in temperature, at a lower temperature, ignition occurred, while at a higher temperature, there was no ignition. A solenoid valve was used to open and close gas lines. A pressure transducer was used to record the pressure during the intake and combustion of the gas. A Pd foil 80 mm long, 1 mm wide and 0.066 mm thick was placed in the reactor. The Pd foil was used both to ignite the flammable mixture and to evaluate the heating of the wire as an arm in a resistance bridge. Before each experiment, the reactor was pumped out to 0.01 Torr, and after each ignition, pumping was continued for 1.5 h to remove most of the water vapour. The total pressure in the reactor was monitored by a vacuum gauge, and the pressure in the buffer volume was controlled by a manometer. Chemically pure gases and 99.85% Pd were used. XPS measurements were performed using a Kratos AXIS Ultra DLD instrument. The microstructure of Pd foils was examined using a Zeiss Ultra Plus ultra-high-resolution field emission scanning electron microscope equipped with an INCA 350 Oxford Instruments console for X-ray microanalysis.

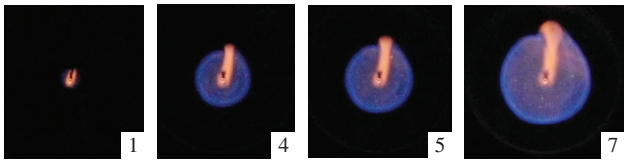

Figure 4 The high-speed colour shooting of initiation by palladium wire and flame propagation in (60% CH_4 + 40% H_2) + air mixture (ϕ = 1, total pressure 1.75 atm, initial temperature 174 °C, frame rate 600 s^{-1}). The number in each frame corresponds to the sequence number of the video image during ignition.

It follows from the above that ignition over the palladium surface near the ignition limit, measured with a bottom-up approach in temperature, provides etching and a corresponding increase in Pd surface area [see Figure 3(*b*),(*c*)]. This leads to an acceleration of the surface reaction of H_2 oxidation and hence the overall process. Each subsequent ignition causes a further increase in the catalytic surface area, so the values of ignition delay (induction) period τ first decrease with decreasing temperature and then increase until the 'lower' temperature limit of ignition is reached.

In summary, the ignition delay (induction) period τ during the combustion of (70–40% hydrogen + 30–60% propane) + air mixtures (τ = 1) over palladium at a total pressure of 1–2 atm first decreases with a decrease in temperature and then increases until the ignition limit is reached, *i.e.*, the NTC phenomenon occurs. The effective activation energy E of the process is 2.2 ± 1 kcal mol^{-1} that is characteristic of a surface process. Therefore, the NTC phenomenon detected in this work is closely related to the Pd surface state. In the sample treated with ignitions, defects in the form of holes were found, which are focused on the etching patterns. In this process, PdO particles are formed during the oxidation of the Pd surface and decompose to Pd and O_2 at the temperature of flame products. Thus, Pd is consumed in the chemical etching reaction with active combustion intermediates. It should limit the applicability of palladium in ignition devices.

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