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The features of hydrogen ignition over Pt and Pd foils at low pressures

Nikolai M. Rubtsov,*[a] Victor I. Chernysh,[a] Georgii I. Tsvetkov,[a] Kirill Ya. Troshin,[b] Igor O. Shamshin[b] and Alexander P. Kalinin[c]

[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 Institute of Chemical Physics, Russian Academy of Sciences, 119991 Moscow, Russian Federation*
[c] *A. Yu. Ishlinsky Institute for Problems in Mechanics, Russian Academy of Sciences, 119526 Moscow, Russian Federation*

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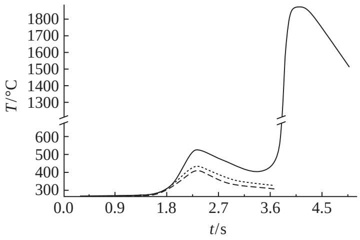
In experiments on $2H_2 + O_2$ ignition over Pd and Pt foils at P_0 = 40–180 Torr and T_0 = 20–288 °C, it has been shown that the temperature of the initiated ignition over heated Pd foil is ~100 °C lower than that over heated Pt foil; even the minimum temperature is already enough to ignite the mixture. The activity of Pd foil expresses itself both in the dark catalytic reaction and in the occurrence of local ignition centers on the foil, from which combustion wave propagates.



It is known that catalytic hydrogen combustion boilers operate at relatively low temperatures and can generate heat for household applications without CO_2 and NO_x emissions.[1,2] Thus, the design of catalysts for hydrogen combustion becomes important. Catalysts for hydrogen combustion should possess properties such as capacity for oxygen storage, thermal stability and should provide hydrogen and oxygen activation, which can be attained with noble metals in support. Noble metals have strong capability of adsorbing hydrogen and oxygen at low temperatures.[3,4] Recently, Borguet *et al*.[3] reported high hydrogen adsorption capacity and low H_2 dissociation temperature on palladium. Moreover, understanding H_2 and O_2 behaviors on the catalyst surface is crucial to focus on the mechanisms of commercialized processes such as preferential oxidation and H_2 combustion.

In addition, the airship fabric bag emissions of dilute hydrogen can be used in a power generation system by low temperature catalytic combustion technology. Due to the low pressure in the stratosphere, the application of catalytic combustion in stratospheric airship power generation systems provides advantages over the conventional technology of low ignition temperature under lean combustion conditions, low pollution emissions, high combustion efficiency and stability.[5,6] Exothermic energy obtained from the hydrogen catalytic combustion reaction can be provided to the power generation system as a heat source, which avoids carrying additional fuels into the stratosphere. For the low temperature catalytic combustion of hydrogen, noble metal catalysts such as palladium and platinum drew significant attention because of their high catalytic combustion activity and a relatively simple preparation method.[7] In the stratosphere, the pressure is between 5.5 and 1.2 kPa.[8] The H_2 reaction kinetics at low and atmospheric pressures differ from each other. Consequently, it is important to find out the difference.

Note that noble metals form oxides which, depending on the reactivity, determine both the speed and the mechanism of catalytic process; it markedly complicates the optimization of catalysis conditions. For instance, Pd transforms to PdO at temperatures lower than 820 °C, and very unstable PtO_2 can hardly be generated below 500 °C. Because of greater stability of PdO in comparison with PtO_2, in the case of Pd catalyst, the active phase is PdO, whereas in the case of Pt, the active phase is metallic Pt. In methane combustion, the activity of PdO is greater than that of Pt, which results in higher conversions for PdO.[9]

We have shown recently that, in the reaction of hydrogen combustion, metallic Pt acts as a heat source similar to a tungsten wire heated by an external source. Obviously, Pt is heated with an internal source, namely, a surface catalytic reaction. The composition of the surface layer changes during ignitions from PtO_2 to another composition, exhibiting properties different from those of PtO_2.[10] We also observed cellular combustion regimes of 40% H_2–air mixture in the presence of Pt wire at 270–350 °C,[11] which were caused by the catalytic action of Pt-containing particles formed upon decomposition of volatile platinum oxide in the gas phase.

Even against that background, the peculiarities of ignition of H_2 over Pt and Pd at low pressures remain not clear enough. This work was focused on experimental studies of low-pressure hydrogen combustion over Pd and Pt foils at total pressures from 10 to 180 Torr and initial temperatures of 20–288 °C.

The experiments were performed with stoichiometric gas mixtures $2H_2 + O_2$. Two reactors were used. Reactor I was a quartz cylinder 12 cm high and 8 cm in diameter with a removable CsI window at the butt-end of the cylinder, inlets for gas blousing, pumping out and ignition of gas mixture [Figure 1(*a*)]. The CsI optical window (35 mm in diameter and 5 mm thick) withstands only five impacts of ignitions at 40 Torr. Reactor II was a quartz one 4 cm in diameter and 30 cm long heated up with an electric furnace, and the temperature was controlled by a thermocouple. The reactor was supplied with a removable quartz window on its butt-end [Figure 1(*b*)]. Reactor I was used for studying the initiated ignition, which was provided by heating Pd or Pt foils (0.06 mm thick 80 mm long and 1 mm wide). Thermal ignition over these foils was studied in reactor II. High-speed recording

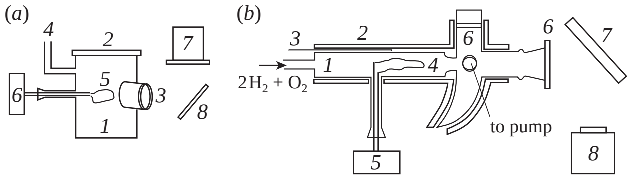


Figure 1 Experimental installations: (*a*) for the study of initiated ignition, (*1*) quartz cylinder 12 cm high and 8 cm in diameter, (*2*) quartz vacuum cover, (*3*) CsI window, (*4*) to the pump, (*5*) Pt/Pd foil, (*6*) foil heater, (*7*) infrared Flir 60 IR camera, and (*8*) rotating mirror; (*b*) for the study of thermal ignition, (*1*) quartz reactor of 4 cm in diameter and 30 cm long heated up in the electric furnace, (*2*) heater, (*3*) thermocouple, (*4*) Pt/Pd foil, (*5*) ADC computer based system, (*6*) optical window, (*7*) rotating mirror, and (*8*) Casio F1 Exilim Pro high-speed digital camera.

of ignition dynamics was carried out from the butt-end of reactor II with a video camera (frame frequency, 600 frames s^{-1}), sensitive in the spectral range of 420–740 nm. An infrared camera (frame frequency 60 frames s^{-1}, 320×240 pix, sensitivity interval 8–14 μm) was used to determine the dynamics of change in temperature of Pt and Pd foils before ignition. A video recording was turned on at an arbitrary moment before initiation. A video file was stored in computer memory and its time-lapse processing was performed. The pumped and heated reactor II was filled with the gas mixture from a high-pressure buffer volume to necessary pressure. In reactor I, the foils were quickly heated to ignite the flammable mixture; in reactor II, the resistance of the foils during thermal ignition was measured. The temperature of the foil during ignition was estimated by an ADC based acquisition system taking into account the temperature dependence of metal resistivity in the computer program. Before each experiment, the reactor was pumped down to 10^{-2} Torr. Total pressure in the reactor was monitored with a vacuum gauge, and the pressure in the buffer volume was monitored with a manometer. Chemically pure gases, 99.99% Pt and 99.9% Pd were used.

Temperatures of ignition of $2H_2 + O_2$ mixture over heated foils of both Pt and Pd were determined. Typical experiments at a total pressure of 40 Torr are shown in Figure 2. It is essential that, after previous ignition, the water vapor should be completely pumped out from the reactor prior to the next run; otherwise, the ignition may not happen. In this case, when heating the foil, the total pressure in the reactor decreases by one third without explosion; *i.e.*, the reaction proceeds completely.

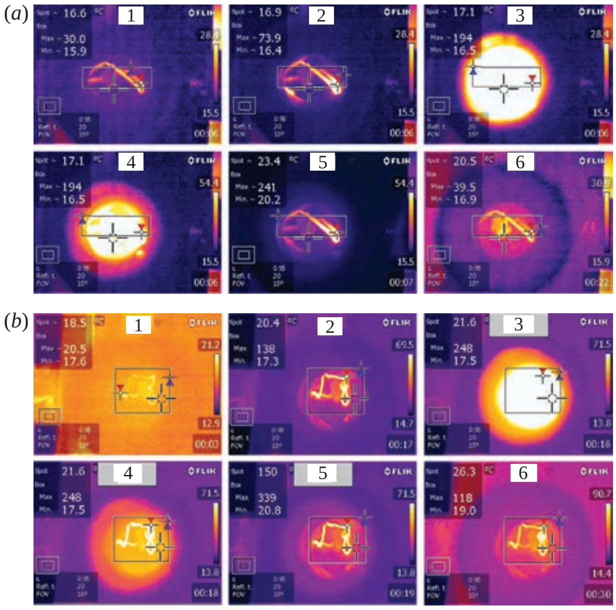


Figure 2 Investigation of initiated ignition by means of the IR camera. (*a*) Over heated Pd foil (60 frames s^{-1}, T_0 = 20 °C, P_0 = 40 Torr). Time in seconds is given at the bottom-right of each frame. Red and blue triangles show the maximum and minimum temperatures in the rectangle, cross indicates the temperature at the point. The emissivity factor is set equal 0.95. (*b*) Over heated Pt foil (60 frames s^{-1}, T_0 = 20 °C, P_0 = 40 Torr).

Note that, for Flir 60, the temperature indicator is slightly delayed as compared with filming; therefore, the maximum temperature T_{exp} = 194 °C (shown on the top left of each frame) in the third frame of Figure 2(*a*) corresponds to that of the foil immediately before ignition; the temperature in the fifth frame (T_{exp} = 241 °C) corresponds to that of the foil heated with the flame. Analogously, in Figure 2(*b*): the maximum temperature in the third frame (T_{exp} = 248 °C) corresponds to that of the foil immediately before ignition; the temperature in the fifth frame (T_{exp} = 339 °C) corresponds to that of the foil heated with the flame.

An emissivity factor in these experiments was 0.95 (close to blackbody one). The recommended emissivity factor over the range 8–14 μm for Pd foil is ~0.05 (http://www.zaoeuromix.ru/) or 0.05–0.1 (http://www.thermalinfo.ru/) for Pt foil. We took an estimated value of 0.07 for both foils. Thus, the actual temperature before ignition of $2H_2 + O_2$ mixture at 40 Torr can be estimated from Stefan–Boltzmann law: $0.95T_{\mathrm{exp}}^4 \approx \approx 0.07T_{\mathrm{act}}^4$ for both foils. We get an ignition temperature of 623 °C and heated foil temperature of 714 °C for Pd foil; the values for Pt foil are 727 and 903 °C, respectively. The obtained ignition temperature of Pt foil is larger than that measured at 1 atm by other means[10] (584 °C). It is related to different conditions of heat losses and heterogeneous chain termination (see below). Even the minimum temperature value (584 °C) is already enough to ignite a 40% H_2 + air mixture;[12] *i.e.*, the influence of the catalytic $H_2 + O_2$ reaction over noble metals is essentially negligible in case of initiated ignition.

It was found that the thermal ignition of $2H_2 + O_2$ over both foils is missing up to 100 Torr. Thus, the usage of a CsI optical window and the IR camera does not make any sense because of the risk of the device damage with CsI splinters in case of ignition. However, in the experiments without ignition, we observed that, at 100 Torr of $2H_2 + O_2$, Pd foil gets heated by ~60 °C using the ADC based acquisition system accounting for the temperature dependence of metal resistivity [Figure 1(*b*)]. At the same time, the total pressure in the reactor decreases by one third for ~3 s, indicating that the hydrogen oxidation is fully completed. Pt foil heats up only by ~10 °C and no consumption of the initial flammable mixture is observed. It means that, at pressures < 100 Torr and T_0 < 300 °C, Pt foil shows no prominent catalytic properties in contrast to Pd foil.

For the spatial development of ignition of $2H_2 + O_2$ mixture at pressures up to 180 Torr and 290 °C over both foils, it was shown that the thermal ignition over Pt foil is missing at 180 Torr and 288 °C. We reported earlier[10,11] that the thermal ignition of 40% H_2 + air mixture at 1 atm already occurs at 260 °C in the reactor 140 mm in diameter. Thus, at lower pressures the heterogeneous chain termination on the reactor walls as well as heat losses are markedly pronounced despite the catalytic activity of the surface. Indeed, using the Einstein–Smoluchowski equation $x^2 = 2D\tau$ (x is a mean diffusion path of a probe particle for a time τ, and D is diffusivity close to thermal conductivity), we get $t_1/t_2 = x_1^2/x_2^2$, where the subscripts 1 and 2 refer to the reactors of different diameters. The computation of wall termination effects in gas-phase radical reactions was described in detail.[13] We give only estimates. In this work x_1 = 2 cm, in ref. 10 x_2 = 7 cm, then t_1/t_2 = 4/49. This value is still less for atmospheric pressure.[10] Therefore, the mean time for a particle to reach the wall in the reactor with a smaller radius at a total pressure of 180 Torr is much less than that for the reactor with a radius of 7 cm at 1 atm. The same applies to heat losses.

The typical sequence of frames of the thermal ignition over Pd foil at 180 Torr and 288 °C is shown in Figure 3. In accordance

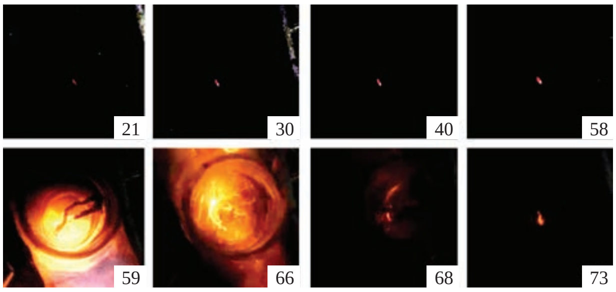


Figure 3 High-speed filming of the thermal ignition of a $2H_2 + O_2$ mixture, 600 frames s^{-1}, $T_0 = 288\,°C$, $P_0 = 180$ Torr.

with published data,[10,11] Pd foil becomes red-hot before and after ignition due to catalytic reactions on Pd surface, the delay period of ignition makes 4 ± 0.3 s. Since Pd foil is not heated up uniformly (see frames 21–58 in Figure 3), the temperature measured by means of Pd foil is a lower boundary of the real temperature of the ignition center, which ignites the combustible mixture. Indeed, it takes a certain time to warm up an entire wire; therefore, the temperature values obtained are underestimated.

At 288 °C and pressures <180 Torr, the ignition is missing. However, total pressure in the reactor decreases by one third for ~ 3 s, indicating that the hydrogen oxidation is fully completed. It means that, at pressures of >100 Torr, the catalytic activity of the Pd surface is high as compared to Pt foil. The monitoring of warming-up kinetics using the temperature dependence of resistance in $2H_2 + O_2$ by means of ADC computer based acquisition system is shown in Figure 4. According to Figures 3, 4, the activity of Pd foil expresses itself in both the occurrence of local ignition centers on the foil, from which combustion wave propagates (see also Figure 2[10]), and the dark catalytic consumption of the flammable mixture, which complicates catalytic reaction proceeding owing to consumption of initial flammable gas. The preheating catalytic process is observed over both foils. At 180 Torr over Pd foil (Figure 4, curve *1*), the catalytic process provides thermal ignition; the warming-up is enough to ignite the mixture.[12] Obviously, the value of the warming-up is underestimated because the foil is unevenly heated during ignition (Figure 3). At 150 Torr over Pd foil (Figure 4, curve *2*) and at 180 Torr over Pt foil, the warming-up during preheating is much lower, and it is not enough to provide the ignition of $2H_2 + O_2$ mixture.[12] The measured warming-up at ignition of this mixture (~1900 °C) agrees well with the literature data accounting for both heterogeneous chain termination and heat losses in the reactor of comparatively small diameter (4 cm).[12]

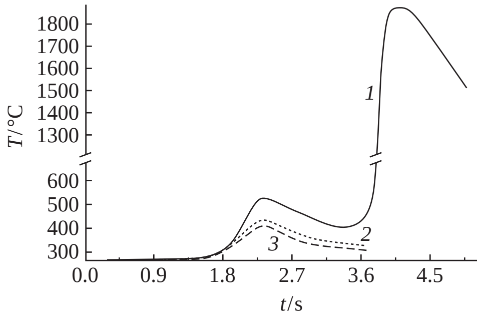


Figure 4 Measurement of warming-up by the dependence of resistance on temperature in $2H_2 + O_2$ using ADC computer based acquisition system. (*1*) Pd foil, $T_0 = 288\,°C$, $P_0 = 180$ Torr, ignition occurred; (*2*) Pd foil, $T_0 = 288\,°C$, $P_0 = 150$ Torr, no ignition; (*3*) Pt foil, $T_0 = 288\,°C$, $P_0 = 180$ Torr, no ignition.

Thus, in the experiments on $2H_2 + O_2$ ignition over Pd and Pt foils at total pressures of 40–180 Torr and $T_0 = 20–288\,°C$, the temperature of the foils during ignition was measured by both an infrared camera and an ADC based acquisition system accounting for the temperature dependence of the metal resistivity. It was shown that the temperature of the initiated ignition at 40 Torr over heated Pd foil is ~100 °C lower than over Pt foil. Even the minimum temperature value (623 °C) is sufficient to ignite a $2H_2 + O_2$ mixture; *i.e.*, the influence of a catalytic $H_2 + O_2$ reaction over the noble metals is negligible in case of initiated ignition. The presence of water vapor prevents ignition. For thermal ignition at 180 Torr and 288 °C over Pd foil. the catalytic activity of the surface is higher than that over Pt foil. The activity of Pd foil reveals itself in both the occurrence of local ignition centers on the foil, from which combustion wave propagates, and the dark catalytic reaction of consumption of the flammable mixture.

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