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Ignition of hydrogen–methane–air mixtures over Pd foil at atmospheric pressure

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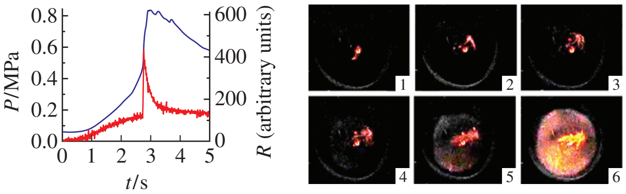
The ignition temperature of a mixture of 40% H_2 in air over Pd (70 °C, 1 atm) is ~200 °C lower than that over a Pt surface (260 °C, 1 atm). In addition, Pd foil ignites mixtures (30–60% H_2 + 70–40% $CH_4)_{stoich}$ + air; Pt foil cannot ignite these up to 450 °C. The effective activation energy of ignition over Pd was estimated at ~3.5 kcal mol^{-1}.



Catalytic combustion of methane and other hydrocarbons is a promising technology for the reduction of air pollution emissions. Considerable efforts have been devoted to the development of catalytic combustors for gas turbine application. Lean-burn gas turbines have been developed worldwide.[1] The problem of ensuring hydrogen safety at the nuclear power plants by means of catalytic afterburners is also of current importance.[2] Noble metals are the most active catalysts for the complete oxidation of hydrocarbons.[3] The platinum-based catalysts are not very efficient in converting methane, the most stable hydrocarbon. This paper considers palladium in providing higher methane conversion. Oxidation catalysts containing Pd can be efficient in converting methane.[4] Palladium is considered the most active catalyst, as compared with other noble metals.[5] In addition, palladium presents a unique temperature self-control capability because of the PdO/Pd transformation.[6] The addition of hydrogen to the initial mixture containing methane can reduce the ignition temperature over Pd, which appears more efficient than in the case of platinum.[5–8]

Previously, we have observed[9] cellular combustion regimes of a 40% H_2 + air mixture in the presence of Pt wire at 270–350 °C. The oxidation regimes are caused by the catalytic action of Pt-containing particles formed by decomposition of volatile platinum oxide in a gas phase. We have also found[8] that, in the combustion of hydrogen, metallic Pt acts as a heat source being heated with an internal source, namely, a surface catalytic reaction. The composition of the surface layer changes during ignitions from Pt dioxide to another one, exhibiting properties different from PtO_2.

Recently,[10] it was found that the initiated temperature of ignition at 40 Torr over heated Pd foil is ~100 °C lower than that over Pt foil; the influence of a catalytic H_2 + O_2 reaction over noble metals is negligible in case of initiated ignition. Upon thermal ignition at pressures up to 180 Torr at 288 °C, the catalytic activity of the pad surface was higher than that of the Pt foil surface. Under these conditions, the activity of Pd foil expresses itself both in the occurrence of local ignition centers on the foil, from which combustion wave propagates, and in the consumption of a flammable mixture in a dark catalytic reaction; the dark catalytic reaction was not observed on the Pt surface under conditions of the experiment.

The aim of this work was to investigate the combustion of hydrogen–methane–air mixtures over Pd at atmospheric pressure in order to estimate Pd efficiency in ignition of the mixtures relative to metallic Pt and to compare the peculiarities of ignition over Pd foil at lower pressures and 1 atm.[†]

The results of the simultaneous detection of changes in pressure and Pd resistance during the ignition of 20% H_2 + air mixture at 90 °C are shown in Figure 1(*a*). The total pressure in the reactor was 1 atm prior to the moment of ignition, *i.e.*, the ignition occurred upon completion of gas inlet. The Pd foil was not heated up uniformly [Figure 1(*b*), frames 1, 2]; therefore, the time dependence of resistance (which represents arbitrary temperature) is somewhat delayed as relative to video recording. The break in that dependence curve corresponds to the resistance at the moment of ignition.

[†] The experiments were performed with stoichiometric gas mixtures of (20–60% H_2 + 80–40% $CH_4)_{stoich}$ + air (stoichiometry composition was calculated for the sum of fuels) and 6–40% H_2 + air at 70–350 °C. A heated cylindrical stainless steel reactor 25 cm in length and 12 cm in diameter equipped with demountable covers and an optical sapphire window in a cover was used[10] (Figure S1, see Online Supplementary Materials). The recording was performed with a Casio Exilim F1 Pro color high-speed camera (frame frequency, 600 s^{-1}). A video file was stored in computer memory and its time-lapse processing was performed.[9,10] The pumped and heated reactor was quickly filled with the gas mixture from a high-pressure buffer volume to a necessary pressure using an electromagnetic valve. A pressure transducer recorded pressure in the course of gas intake and combustion. A Pd foil 60 mm long, 1 mm wide and 0.06 mm thick was placed in the reactor. For comparison, Pt foil of the same size was used in some experiments. The Pd foil was used both to ignite the flammable mixture and to measure the temperature of the foil as a bridge arm. Before each experiment, the reactor was evacuated to 0.1 Torr. Total pressure in the reactor was monitored with a vacuum gauge, and the pressure in the buffer volume was controlled with a manometer. Chemically pure gases, 99.99% Pt and 99.85% Pd were used.

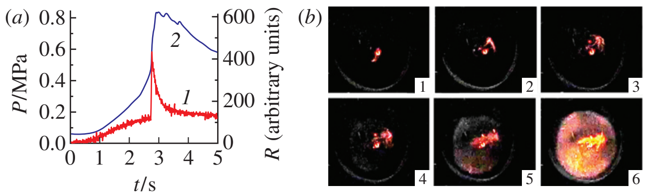


Figure 1 (*a*) Simultaneous monitoring of the changes in (*1*) pressure and (*2*) Pd resistance during the ignition of a 20% H_2 + air mixture, 100 °C. (*b*) High speed color detection of the initiation and flame propagation in 20% H_2 + air mixture with a palladium wire, 600 s^{-1}. Numbers in each frame correspond to the consecutive numbers of video images during the ignition.

Thus, 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 the wire; therefore, the resistance values (arbitrary temperature) obtained by the method are underestimated. The main experimental result is that the ignition temperature of a mixture of 20% H_2 + air over Pd (90 °C, 1 atm) is at least ~170 °C lower than that over the Pt surface (260 °C, 1 atm, 40% H_2 + air).

Spatial development of ignition and flame propagation of a 20% H_2 + air mixture at $P_0 = 1$ atm was investigated over Pd foil [see Figure 1(*b*)]. Just like in the case of Pt, the Pd foil becomes red-hot before and after ignition due to catalytic reactions on the Pd surface. In the presence of the Pd foil, the cellular structure of the flame front is not observed, as compared with the results obtained on the Pt surface.[9] This is due to the greater stability of PdO in comparison with PtO_2, which is very unstable and decomposes over 500 °C.[6]

The time dependences of the resistance of the Pd foil on Pd initiated ignition of 20% H_2 in air at $P_0 = 1$ atm at temperatures of 90, 100, and 107 °C are shown in Figure 2. One can see that the difference between initial temperatures for *e.g.* 90 and 107 °C, which is ~20 °C, comprises ~20 arbitrary units; the difference between initial temperature and the temperature of ignition at 1.9 s (107 °C) makes ~280 arbitrary units. The difference between initial temperature and the temperature of ignition at 2.2 s (100 °C) makes ~230 arbitrary units. The variation in the values is due to the fact that the Pd foil is not heated up uniformly; therefore, the temperatures of the local centers of ignition can differ a little from each other. Thus, the lower temperature increase could be estimated at (20 °C × 280/20) ≈ 280 °C for a reactor temperature of 107 °C; *i.e.*, the lower limit of the temperature of ignition is ~387 °C. For a reactor temperature of 100 °C, the lower value of temperature increase could be estimated at (20 °C × 230/20) ≈ 230 °C; *i.e.*, the lower limit of the temperature of ignition is ~330 °C. Thus, although the value of 387 °C almost coincides with the conclusion that Pd acts as a heat source similar to a nichrome wire heated by an external source,[11] the other values of the lower limit obtained are smaller than those for Pt wire,[9] these are also less than the temperature limit of the stoichiometric mixture $2H_2 + O_2$ at 1 atm.[12] It means that a surface catalytic reaction can play a certain role in the ignition.

To bring out the contribution of surface reactions (including those responsible for the heating of the Pd foil), the temperature dependence of hydrogen concentration at the explosion limit was experimentally determined. Explosion limits of stoichiometric gas mixtures of 6–40% H_2 + air (indicated with crosses) and (20–60% H_2 + 80–40% CH_4)$_{stoich}$ + air at 70–350 °C are presented in Figure 3(*a*). The Pd foil ignites 40% H_2 + air mixture in the reactor, which is heated only to 70 °C. To compare, the ignition of the same mixture with Pt wire requires heating to 260 °C.[9] Moreover, as can be seen in Figure 3, the minimum concentration of H_2 at the limit is about 5%, which is very close to the concentration ignition limit of H_2 at room temperature at spark initiation.[11,12] Therefore, CH_4 in H_2–CH_4–air mixtures reacts only in a gaseous phase rather than on the Pd surface. Note that Pt foil of the same size at reactor temperatures to 450 °C does not ignite the above H_2–CH_4–air mixtures.

On the contrary, Pd foil ignites mixtures (30–60% H_2 + 70–40% CH_4)$_{stoich}$ + air [empty circles in Figure 3(*a*)]. However, we did not manage to ignite the mixture (20% H_2 + 80% CH_4)$_{stoich}$ + air with Pd foil at temperatures up to 450 °C, probably, because H_2 concentration in the mixture (2.2%) is lower than the concentration ignition limit of H_2.[12]

The temperature dependence of the H_2 fraction in the flammable mixtures in the Arrhenius coordinates is shown in Figure 3(*b*). It can be approximated by a straight line (the correlation coefficient is 0.98). The data were processed with the use of the Statistica 9 program package.

Based on Figure 3(*a*), we can conclude that the dependences for H_2–CH_4–air and H_2 + air mixtures fall practically on a single curve. We can assume that the dependences are determined with only H_2 fraction in the mixture. Note that we limited ourselves to 40% H_2 in the mixture because the reaction of hydrogen oxidation slows down upon a further increase in the H_2 content.[12,13] For that reason, the effective activation energy obtained below is only an estimated value.

The experimental effective activation energy of the process is $E = 3.5 \pm 1$ kcal mol^{-1}, which is characteristic of surface processes.[14] This value is close to activation energies of hydrogen adsorption–desorption on Pd.[15] However, to provide the ignition, a cycle of reactions in which branching (an increase in the number of active centers) takes place must occur.[13] The activated ($E = 16.7$ kcal mol^{-1})[12,13] homogeneous branching step $H + O_2 \rightarrow O + OH$ is the slowest elementary reaction of the cycle. Therefore, the activation energy of the branching should determine the temperature dependence of the overall process, as it takes place in similar experiments with Pt metal.[9] It means that in case of Pd, the branching step has probably heterogeneous nature because the effective activation energy is close to $E \sim 3.5$ kcal mol^{-1}.

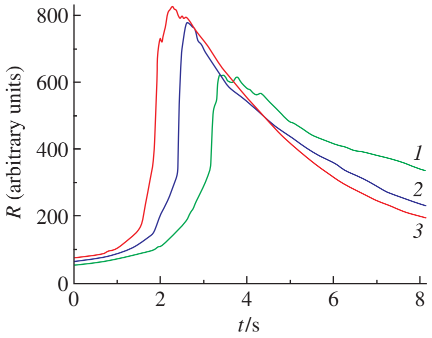


Figure 2 The time dependences of the Pd foil resistance at Pd initiated ignition of 20% H_2 + air mixture: (*1*) 90, (*2*) 100 and (*3*) 107 °C. $P_0 = 1$ atm.

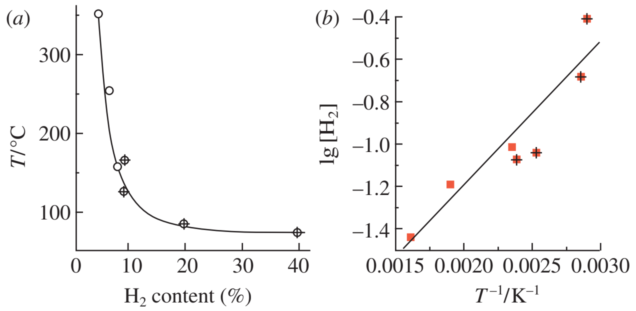


Figure 3 (*a*) Experimental dependence of temperature at the ignition limit on H_2 content in the H_2–air and H_2–methane–air mixtures; crosses indicate H_2–air mixtures; (*b*) Arrhenius plots of the dependence.

Thus, we experimentally found that the ignition temperature of 40% H_2 in air over Pd (70 °C, 1 atm) is ~200 °C lower than that over the Pt surface (260 °C, 1 atm). In addition, Pd foil ignites mixtures (30–60% H_2 + 70–40% CH_4)$_{stoich}$ + air, whereas Pt foil cannot ignite these up to 450 °C. It means that Pd foil is more effective than the Pt foil.

The cellular structure of a flame front at ignition with Pd foil is not observed, as compared with the results obtained over Pt surface. Therefore, Pd seems to be more usable for hydrogen recombinators employed at the nuclear power plants because no catalytic particles formed by decomposition of volatile oxide can appear in gas phase as ignition centers, as compared to Pt.

The estimated effective activation energy of the process is 3.5±1 kcal mol^{-1}, which is characteristic of surface processes. It indicates the noticeable role of the dark reaction of H_2 and O_2 consumption observed directly at low pressures. The occurrence of that reaction reduces the probability of accidental explosion in Pd-initiated oxidation, as compared with Pt.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.07.039.

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