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Ignition of hydrogen–air mixtures over Pt at atmospheric pressure

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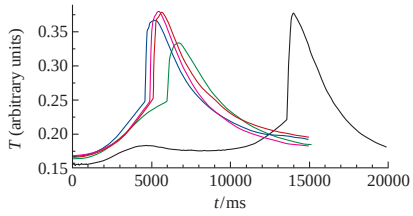
It is shown that metallic Pt acts mainly as a heat source in the reaction of hydrogen combustion. The composition of the surface layer changes during ignitions (from PtO_2 to the composition exhibiting properties different from PtO_2).



The catalytic chemistry of hydrogen oxidation over noble metals has been studied.[1,2] However, for coupled heterogeneous and homogeneous combustion systems, there are only a few published results (especially, at elevated pressures) related to hydrogen and hydrogen-containing fuels. The homogeneous ignition of fuel-lean and fuel-rich H_2–air mixtures over Pt-coated stagnation flow surfaces was investigated at atmospheric pressure by Bui *et al.*,[3] who established the impact of an equivalence ratio on the ignition temperature. It is essential to ascertain the operating conditions (pressure, mixture preheat, catalytic wall temperature, reactor geometrical confinement and residence time) under which gas-phase chemistry plays a major role, given the growing interest in catalytic combustion systems with the use of either hydrogen or hydrogen-enriched fuels.[4,5]

Catalytic ignition and the related extinction and instability phenomena are of practical importance, *e.g.*, in car exhaust catalysis,[6] catalytic afterburning,[7] chemical reactors and catalytic combustion.[8] Catalytic ignition is also of purely scientific interest as an incompletely understood critical phenomenon, where the system undergoes a transition from one steady state essentially controlled by surface reaction kinetics to another steady state primarily controlled by mass transport.[9] Due to the nonlinear coupling of kinetics, mass and heat transport, the same system exhibits not only ignition but also[10] oscillatory and chaotic behavior. In addition, the ignition can yield information about rate constants. Two experimental techniques are commonly employed, namely, a heated wire technique and a heated gas technique.[11] As stated by Rinnemi *et al.*,[12] ignition is determined by the coupling of preignition surface reaction kinetics and heat losses. The heated wire technique has been used.

We have recently observed[13] cellular combustion regimes of a 40% H_2–air mixture in the presence of Pt wire over a range of 270–350 °C. The regimes were caused by the catalytic action of Pt-containing particles formed by the gas-phase decomposition of volatile platinum oxide. As is well known,[14] a thin film of feebly stable solid platinum forms on platinum surfaces in air or oxygen at room temperature and thickens as the temperature is raised to about 500 °C, when it decomposes. The weight loss of platinum at higher temperatures is attributed to the formation of gaseous platinum oxide and the deposition of platinum on cooler surfaces (above 500 °C) to its disproportionation. It means that both Pt oxide and Pt metal in the form of molecules or clusters exist in a gaseous phase at temperatures over 500 °C.

Thus, the description of the ignition of H_2 over a Pt surface should take into account both the heating of the Pt surface probably to the temperature of thermal ignition due to the catalytic reaction of H_2 oxidation and the desorption of chain carriers from the surface as a result of the same surface reaction. The contribution of one of these processes could be much lower than that of another one. Indeed, the ignition is observed only if a Pt surface gets red-hot.[15]

This study was focused on the establishment of the comparative contribution of the mechanisms of (i) initiation by a surface reaction leading to desorption of active centers and (ii) initiation of the ignition involving only thermal heating with Pt surface.

Spatial development of ignition of preliminary prepared 40% H_2 + 60% air mixtures at 1 atm pressure over both Pt foil and Pt wire was investigated.† We found out earlier[15] that the temperature of thermal ignition of H_2–air mixtures at 1 atm in the reactor containing Pt foil was ~170 K less than that in the

† The experiments were performed with 40% H_2 + 60% air gas mixtures at 270–350 °C. A heated cylindrical stainless steel reactor 25 cm in length and 12 cm in diameter was equipped with demountable covers and an optical quartz window in one of the covers (Figure S1, Online Supplementary Materials).[16] The temperature was measured to within 0.3 K. Registration of ignition and flame propagation was performed by means of a Casio Exilim F1 Pro color high-speed camera (the frequency of shots, 600 s^{-1}). A video file was stored in a computer memory and its time-lapse processing was performed.[17] The pumped and heated reactor was quickly filled with the gas mixture from a high-pressure buffer volume to a necessary pressure. An electromagnetic valve was used to open and close gas communications. A pressure transducer recorded pressure in the course of bleeding-in and combustion. Either Pt foil 12 × 6 cm and 0.3 cm thick or a Pt wire 6 cm long and 0.2 cm in diameter were placed in the reactor. The Pt wire was used both to ignite the flammable mixture and to measure the temperature of the wire as a bridge arm. The temperature of the Pt foil during ignition was estimated by a double-beam color pyrometer (Figures S1, S2). Before each experiment, the reactor was pumped down to 0.1 Torr. The total pressure in the reactor was monitored with a vacuum gauge and the pressure in the buffer volume, with a manometer. Chemically pure gases and 99.99% Pt were used.

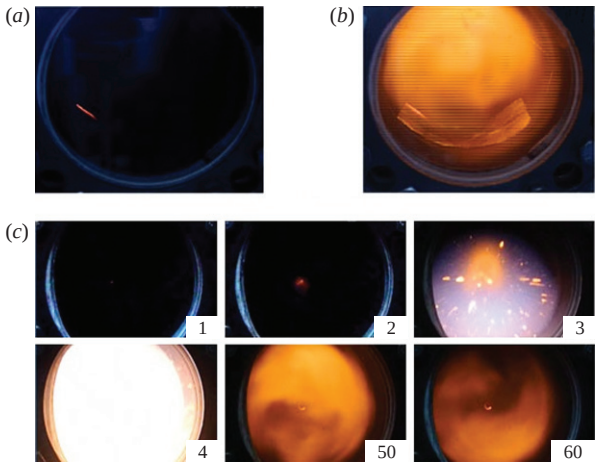


Figure 1 Pt foil in the reactor (*a*) before and (*b*) after ignition (the foil is illuminated with 40% H_2 + air flame). (*c*) High speed color recording of the initiation and FF propagation in 40% H_2 + air mixture with a platinum wire, 600 frames s^{-1}. Numbers in each frame correspond to consecutive numbers of the video images. The first frame is defined by the point when Pt wire becomes red-hot.

stainless steel reactor. However, Pt foil in the H_2–O_2 mixture can be heated up to a temperature higher than that of ignition in a stainless steel reactor; *i.e.*, the temperature of the reactor walls is not the controlling parameter of thermal ignition. Time delays of ignition in the mixtures over Pt foil can reach tens of seconds at a temperature lower than 260 °C in the case of the very first experiment, in which Pt surface has not been treated with active centers of ignition yet.

In the following series of experiments, the Pt foil temperature during ignition was estimated using a two-beam color pyrometer (see Figure S2). Whereas Pt foil is not heated up uniformly [Figure 1(*a*),(*b*)], in the first experiment, the red-hot area of the Pt foil was identified; in the second one, both of the beams were directed at that area to measure the temperature.

Only a discrete ignition center is brought to red heat (a white circle in frames 25 and 40, Figure S2). Since a double-beam color pyrometer measures a temperature value between the beams on the surface in question, the mean temperature of the region between the beams is detected.

The temperature reaches 584 °C at the moment preceding ignition (the ignition is presented in frame 41, Figure S2). This value is evidently a lower boundary of the actual temperature of the ignition center. Indeed, using a color table of metals,‡ the temperature of the active center in frame 40 (Figure S2) could be roughly estimated at ~800 °C; the temperature of the red hot part of the foil [Figure 1(*b*)] is ~730–800 °C. All the values are in good agreement with each other. The minimum temperature (584 °C) is already enough to ignite a 40% H_2 + air mixture.[18]

Thus, based on the results obtained, one can conclude that Pt acts as a heat source similar to a wire heated by an external source. However, in this case, Pt is heated by an internal source, namely, a surface catalytic reaction.

To estimate the role of the surface reaction, in the following series of experiments, a Pt wire was used both to ignite the flammable mixture and to measure the temperature of the wire as a bridge arm (Figure S1). Typical sequences of frames of high-speed recording of a flame front (FF) propagation in the gas mixture initiated with Pt wire are shown in Figure 1(*c*). In frame 3, in the presence of Pt wire, a cellular structure of FF is observed according to published data;[13] Pt wire is red-hot before and after ignition due to catalytic reactions on Pt surface.

‡ See, *Bol'shoi politekhnicheskii entsiklopedicheskii slovar (Large Polytechnic Encyclopoedic Dictionary)*, Multitreid, 2004 (in Russian).

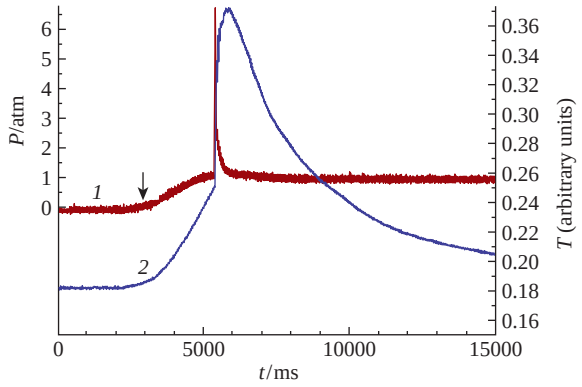


Figure 2 The time dependence of (*1*) pressure and (*2*) temperature (Pt wire, T_0 = 320 °C, P_0 = 1 atm). The arrow shows the beginning of gas admission.

In Figure 2, the oscillogram of the simultaneous registration of signals from the pressure transducer and the Pt wire as a bridge arm is shown. The total pressure in the reactor reaches 1 atm immediately prior to the moment of the ignition. Because the Pt wire, similar to Pt foil, is not heated up uniformly [Figure 1(*c*), frames 1, 2], the temperature measured by means of Pt wire 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 temperature values obtained by the method are underestimated.

Let us estimate the lower boundary temperature sufficient to ignite the combustible mixture. According to time dependences of the temperature for Pt initiated ignition [Figure 3(*a*)], the difference between initial temperatures for *e.g.* 300 °C (curve *2*) and 320 °C (curve *3*) comprises ~0.01 arbitrary units; therefore, the

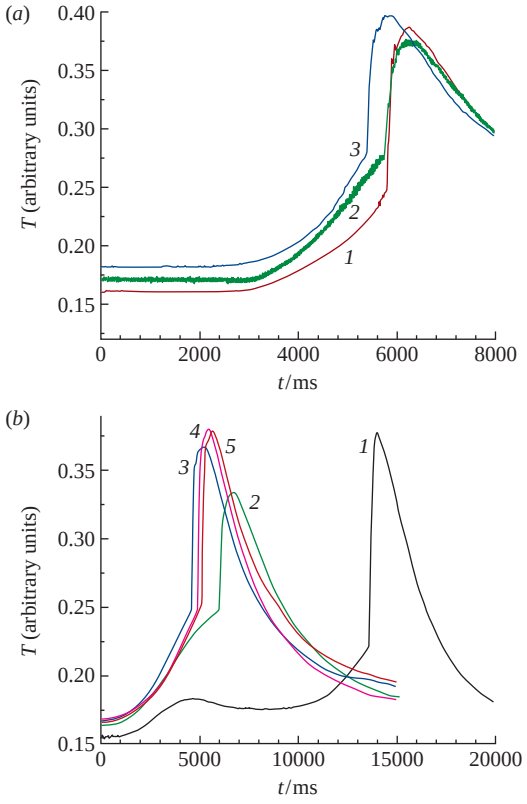


Figure 3 (*a*) The time dependence of the temperature for the Pt initiated ignition of 40% H_2 + 60% air mixture. T_0 is (*1*) 280, (*2*) 300 and (*3*) 320 °C. P_0 = 1 atm. The curves are brought into coincidence for the delay times of ignition differed from each other. (*b*) Dependence of ignition delay of 40% H_2 + 60% air mixture over Pt wire on the number of ignitions (*1–5*). P_0 = 1 atm. T_0 = 304 K.

difference between initial temperature and the temperature of ignition at 5900 ms is ~0.1 arbitrary units. Therefore, the lower boundary temperature could be estimated as 20 °C (0.1/0.01) ~ 200 °C; *i.e.*, the lower limit of the ignition temperature is 500 °C. This value corresponds well to those obtained above; it is also consistent with the above conclusion that Pt acts as a heat source similar to a wire heated by an external source.

However, note that ignition delays τ for the experiments presented in Figure 3(*b*) markedly differ: τ(280 °C) = 35 s, τ(300 °C) = 10 s, and τ(320 °C) = 7.5 s. Thus, as stated above, τ reaches its highest value in the case of the first experiment at 280 °C over 'fresh' Pt surface; the temperature of ignition is 20 °C lower (curve *4*). It means that the surface state of untreated Pt provides the lowest ignition temperature.

In the following experiments, the dependence of the surface state of the Pt wire (starting from the 'fresh' one) on the number of ignitions was studied.

Figure 3(*b*) shows that the highest value of a delay period of ignition was observed in the first experiment; τ values are markedly less converging to a stationary value for Pt surface treated with ignitions. Over a fresh Pt surface, the 40% H_2 + air mixture at the moment 4.5 s is about to ignite; approximately by that moment, the ignition over the treated Pt surface occurs. Over the fresh surface in a time interval between 4.5 and 14 s, the surface somehow reconstructs itself; then, ignition takes place. Moreover, curve *1* is placed lower than the others. It means that the dependence of the resistance on temperature discerns between fresh Pt and treated Pt; *i.e.*, the materials of the fresh Pt wire and a treated one differ markedly. According to published data,[13] the Pt surface before ignition is coated with a layer of PtO_2; after ignition, a fraction of the layer in the form of ultra-disperse particles of Pt dioxide is emitted under heating and spreads over the reactor volume. This suggests that the platinum dioxide layer after the first ignition becomes so thin that it does not have time to be reformed. Thus, the first ignition occurs over a thick layer of Pt dioxide, and the following ignitions proceed over the surface of another composition, which needs further investigation with Auger or X-ray photoelectron spectroscopy methods.

Thus, the obtained results allow one to conclude that, in the reaction of hydrogen combustion, metallic Pt serves as a heat source similar to, say, a tungsten wire heated by an external source. However, in the case under investigation, Pt is heated with an internal source, namely, a surface catalytic reaction. It should be also taken into account that the composition of the surface layer changes during ignitions from Pt dioxide to another composition, exhibiting properties different from PtO_2.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.05.031.

References

1 Y. Ghermay, J. Mantzaras, R. Bombach and K. Boulouchos, *Combust. Flame*, 2011, **158**, 1491.
2 M. Maestri, A. Beretta, T. Faravelli, G. Groppi, E. Tronconi and D. G. Vlachos, *Chem. Eng. Sci*., 2008, **63**, 2657.
3 P. A. Bui, D. G. Vlachos and P. R. Westmoreland, *Proc. Combust. Inst.*, 1996, **26**, 1763.
4 V. Seshadri and N. S. Kaisare, *Combust. Flame*, 2010, **157**, 2051.
5 A. Scarpa, P. S. Barbato, G. Landi, R. Pirone and G. Russo, *Chem. Eng. J.*, 2009, **154**, 315.
6 D. Schweich and J. P. Leclerc, in *Catalysis and Automotive Pollution Control*, ed. A. Crucq, Elsevier, Brussels, 1990, vol. 2, p. 437.
7 T. Schmidt, in *Catalysis and Automotive Pollution Control*, ed. A. Crucq, Elsevier, Brussels, 1990, vol. 2, p. 55.
8 D. L. Trimm, *Appl. Catal*., 1983, **7**, 249.
9 A. Schwartz, L. L. Holbrook and H. Wise, *J. Catal*., 1971, **21**, 199.
10 M. M. Slin'ko and N. I. Jaeger, *Oscillating Heterogeneous Catalytic Systems* (*Studies in Surface Science and Catalysis*, vol. 84), Elsevier, Amsterdam, 1994.
11 S. W. Weller and C. G. Rader, *AIChE J.*, 1975, **21**, 176.
12 M. Rinnemo, O. Deutschmann, F. Behrendt and B. Kasemo, *Combust. Flame*, 1997, **111**, 312.
13 N. M. Rubtsov, A. N. Vinogradov, A. P. Kalinin, A. I. Rodionov, K. Ya. Troshin, G. I. Tsvetkov and V. I. Chernysh, *Mendeleev Commun*., 2016, **26**, 160.
14 J. C. Chaston, *Platinum Met. Rev.*, 1964, **8**, 50.
15 N. M. Rubtsov, B. S. Seplyarskii, K. Ya. Troshin, V. I. Chernysh and G. I. Tsvetkov, *Mendeleev Commun*., 2012, **22**, 222.
16 N. M. Rubtsov, B. S. Seplyarskii, K. Ya. Troshin, G. I. Tsvetkov and V. I. Chernysh, *Mendeleev Commun*., 2011, **21**, 31.
17 N. M. Rubtsov, I. M. Naboko, B. S. Seplyarskii, V. I. Chernysh and G. I. Tsvetkov, *Mendeleev Commun.*, 2014, **24**, 50.
18 B. Lewis and G. von Elbe, *Combustion, Flames and Explosions in Gases*, Academic Press, New York, 1987.

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