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Cellular combustion and delay periods of ignition of a nearly stoichiometric H_2–air mixture over a platinum surface

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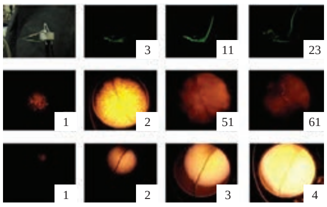
Cellular combustion regime of a 40% H_2–air mixture in the presence of Pt wire at 270–350 °C was observed for the first time. The regime is caused by the catalytic action of Pt-containing particles formed by the decomposition of volatile platinum oxide in a gas phase.



The advancement in catalytically stabilized (CS) combustion technology requires the development of catalysts with improved activity (desired light-off temperature less than 450 °C) and thermal stability, the understanding of catalytic surface processes, the knowledge of low-temperature homogeneous kinetics and their respective coupling with heterogeneous kinetics. The onset of homogeneous ignition within the catalytic reactor is detrimental to the catalyst integrity (it can cause catalyst meltdown) and the knowledge of such an event is of prime interest to CS reactor design. The gas-phase ignition is strongly influenced by hetero/homogeneous coupling (catalytic fuel depletion, radical adsorption/desorption reactions); therefore, its accurate prediction requires the understanding of the ignition mechanism in the presence of a catalyst. The concept of hydrogen-assisted CS combustion is of particular interest.[1] Addition of small amounts of H_2 to natural gas reduces the catalyst light-off temperature and improves the combustion stability by damping flame pulsations. Therefore, the knowledge of hydrogen CS combustion is important in the understanding of hydrogen-assisted CS combustion.

Experimental facts relating to the reactions between platinum (the most effective combustion catalyst) and oxygen at temperatures up to the melting point were considered by Chaston.[2] A thin film of solid platinum oxide (PtO_2 or PtO[3]) forms on platinum surfaces in air or oxygen at room temperature[4] and thickens as the temperature is raised to about 500 °C when it decomposes.[5] The loss of platinum weight at higher temperatures is attributed to the formation of gaseous platinum oxide and the deposition of platinum on cooler surfaces (~ 500 °C) to its disproportionation. Platinum deposits on a furnace brick removed after long service in such a way that black oxide-containing deposits can be seen on the cooler edges and crystalline platinum deposits on the hotter surfaces.[2]

The molecules or clusters of both platinum oxide and platinum metal exist in a gaseous phase over 500 °C. Therefore, Pt-containing particles extending by diffusion into the volume containing combustible gas (H_2–air mixture) in the process of warming up of the Pt wire, are the catalytic centers where hydrogen ignition can occur in the course of flame front propagation. Therefore, one can expect the instabilities of the flame front of hydrogen combustion initiated with Pt wire caused by catalytic centers distributed in the gas phase. This instability should be observed in the absence of thermal diffusion instability (nearly stoichiometric mixtures[8]). The detection of that regime was one of the purposes of this work.

Comparably long delay times of 40% H_2 + air ignition at 1 atm were first observed over a Pt foil.[3] It was established that the ignition of H_2–air mixtures at atmospheric pressure begins with primary center occurrence on the most chemically active site of the surface, which initiates flame propagation.[3] In addition, the introduction of platinum wire into the reactor eliminates the phenomenon of negative temperature coefficient in combustion of stoichiometric *n*-pentane–air mixtures; however, Pt wire has no effect on the ignition delay time of thermal ignition of the mixture at lower temperatures.[6]

The experiments on speed cinematography were performed with gas mixtures of 40% H_2 + 60% air at 270–350 °C without gas swirling (Al ring was inserted into the reactor).[†,6–16]

[†] A heated cylindrical stainless steel reactor 25 cm in length and 12 cm in diameter equipped with tangential gas input, demountable covers and an optical quartz window was used (Figure S1, Online Supplementary Materials).[9–11] The accuracy of temperature measurements was 0.3 K. Registration of ignition and flame propagation was performed by an optical 3D spectrometer (hyper spectrometer) and a Casio Exilim F1 Pro color high-speed camera (the frequency of shots, 600 s^{-1}). A video file was stored in computer memory and its time-lapse processing was performed.[12–14] A 3D spectrometer[15] simultaneously measured both a vertical narrow strip on the test object (a spatial coordinate) and a spectral wavelength with a two-dimensional optical detector array. The process of hyperspectral recording of a combustion process is described elsewhere.[15] The speed video filming of combustion and 3D spectrophotometry were carried

Spatial development of ignition of H_2–air mixtures at 1 atm was investigated. The temperature of ignition of H_2–air mixtures in the reactor containing Pt foil[3] is ~170 K less than that in a stainless steel reactor. Note that the changeover across a critical condition of ignition is accompanied by a substantial growth of the induction period τ only over a Pt catalytic surface, though τ of ignition over stainless steel changes stepwise in a very narrow temperature interval of ~1 K. Induction periods in the mixtures can reach tens of seconds both at temperature less than 260 °C and in the case of ‘fresh’ state of Pt surface. Figure 1 shows the sequences of video images of development of the initial centers of ignition. The smooth uniform flame front (FF) is observed for spark-initiated ignition in 40% H_2 + air mixture at room temperature of reactor walls for stainless steel surface. If the Pt foil is placed in the stainless steel reactor, FF is almost uniform. It agrees with earlier experimental observations[2,4,5] that oxide layer on the bulk Pt is thinner than that on Pt wire, so the amount of Pt containing particles in the volume is too small to influence the FF structure.

The video frames of the heating of Pt wire by current J = 2 A is presented in Figure 1(*c*). The wire was illuminated with a laser sheet. The ultra-disperse particles of Pt oxide are emitted under heating according to published data.[2,4,5] As platinum oxide emission out of the wire is recorded with a frequency of 60 frames per second, it is obvious that in experiment on initiation of hydrogen ignition by a wire in the heated reactor, during a delay period (under our conditions, 3–70 s) ultra-disperse Pt oxide can spread about all of the reactor volume before ignition.

However, in the presence of Pt wire [Figure 1(*d*)] the cellular structure of FF is observed; the Pt wire becomes red-hot before and after ignition due to catalytic reactions on Pt surface. Addition of 15% CO_2 to the combustible mixture completely suppressed the cellular regime of combustion; thus, a 15% additive of helium does not influence the cellular combustion regime.

In the absence of Pt wire, FF of hydrogen combustion under similar conditions is smooth and uniform.[3,17] At temperatures of > 500 °C, the molecules or clusters of both platinum oxide and platinum metal are formed in a gas phase. Thus, the instability found is caused by the Pt-containing particles extending into the reactor volume by diffusion acting as catalytic centers where hydrogen ignition occurs in the course of FF propagation. As distinct from He additives [Figure 1(*f*)], in the presence of CO_2 the diffusivity of catalytic particles decreases and these probably do not influence the propagating flame shape; therefore, FF is uniform [Figure 1(*e*)].

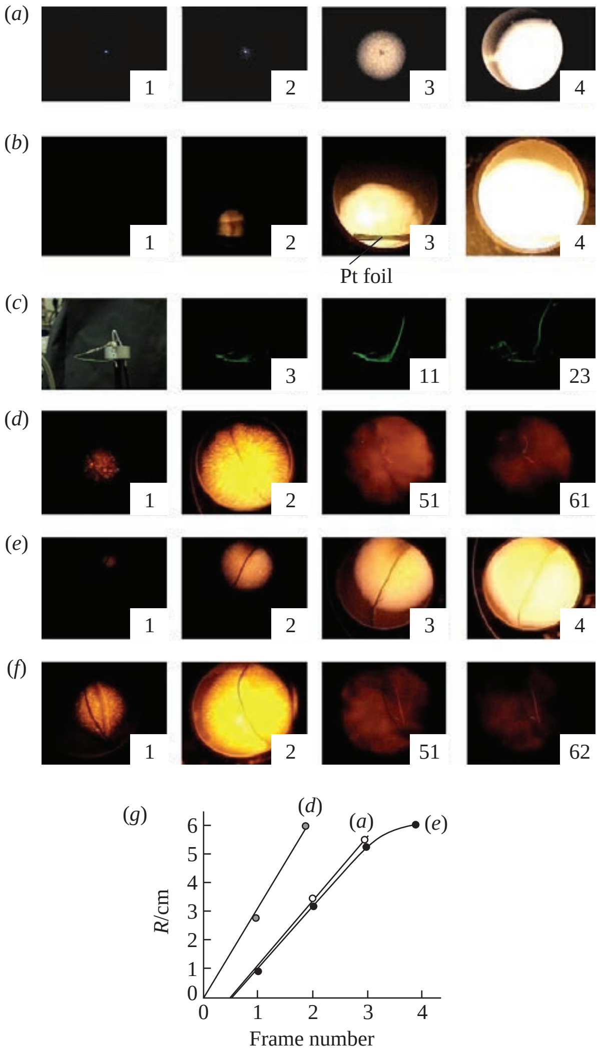


Figure 1 Sequences of video images of spatial development of (*a*) spark initiated ignition in 40% H_2 + 60% air mixture at the reactor walls temperature of 20 °C, 600 shots s^{-1}, P = 1 atm, material of the wall is stainless steel; (*b*) 40% H_2 + 60% air mixture at the reactor walls temperature of 247 °C, Pt foil is placed in the stainless steel reactor, its movement under explosion is clearly seen in shots 75, 100; Pt foil becomes incandescent under the action of reaction products (shots 145–170); (*c*) the heating of Pt wire (J = 2 A); the wire is lighted with a vertical green laser sheet, 60 frames s^{-1}; (*d*) 40% H_2 + 60% air mixture at the reactor walls temperature of 316 °C; Pt wire is placed in the stainless steel reactor (shots 1, 61); Pt wire is heated before explosion and after it due to catalytic reactions (shots 1, 61); (*e*) 85% (40% H_2 + 60% air mixture) + 15% CO_2 at the reactor walls temperature of 320 °C; (*f*) 85% (40% H_2 + 60% air mixture) + 15% He at the reactor walls temperature of 309 °C; Pt wire is placed in the stainless steel reactor (shots 1, 61); Pt wire is heated before explosion and after it due to catalytic reactions (shots 1, 62); P = 1 atm, 600 shots s^{-1}. Numbers in each frame correspond to consecutive number of the video image. (*g*) The dynamics of increase in radius (R) of FFs estimated from the data of Figure 1: experiments (*a*), (*c*), (*d*); P_0 = 1 atm, 600 frames s^{-1}.

In Figure 1(*g*) the estimates of normal flame velocities from the change of a visible flame radius by published equations[9,17] are presented. At spark initiation in the mixture diluted with carbon dioxide, the constant flame velocity is reached in a period corresponding to the time of formation of the steady FF.[17] However, in the presence of the platinum catalyst [Figure 1(*g*)], the constant FF velocity (within an experiment error) is reached practically at once, *i.e.*, the catalytic effect of Pt leads to the sharp reduction of the time of steady FF formation. The normal velocity of FF in the presence of a catalytic surface is much higher (~2.6 m s^{-1}) than that without the catalyst (at spark initiation ~1.9 m s^{-1}, in the presence of 15% of CO_2, ~1.8 m s^{-1}).

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out simultaneously. The pumped and heated reactor was quickly filled with the gas mixture from a high-pressure buffer volume to a necessary pressure. Because of a sharp pressure difference in the buffer volume and the reactor, a gas swirl occurred in the reactor that led to reduction of time of establishment of uniform temperature distribution.[6] To prevent gas swirling, an Al ring focused perpendicular to a gas flow was inserted into reactor. The direct measurements of the dynamics of temperature change in the center of the reactor by thin thermocouples was performed under similar conditions.[7] The time of gas mixture warming up was no longer than 0.3 s. In this case, the formula considering only conductive heat exchange gives a considerably greater value of the order of tens of seconds.[8] A pressure transducer recorded pressure in the course of bleeding-in and combustion. At the moment of valve opening, a light-emitting diode was turned on, and its flash was recorded by the camera. It allowed us to determine a delay time of ignition τ from a shot sequence independently for each separate ignition. Pt foil 12×6 cm and 0.3 cm thick or Pt wire 15 cm long and 0.3 cm in diameter was placed in the reactor. Before each experiment, the reactor was pumped down to 0.1 Torr. For the diagnostics of dust structures, the particles emitted by a platinum wire under heating in atmospheric air were illuminated with a wide flattened laser beam (laser sheet) at λ = 532 nm.[16]

Figure 2 Hypercube of combustion of the 40% H_2–air mixture initiated by a platinum wire obtained with the hyper spectrometer, T_0 = 320 °C, P_0 = 1 atm, a spectral interval of 550–650 nm.

The nonuniformity of FF light emission caused by catalytic instability is detected not only by the high-speed filming (Figure 1) but also by the hyper spectrometer [Figure 2, the experiment in Figure 1(*d*)] directly in a hyper cube. According to Figure 2, light spots (hot spots) corresponding to the combustion cell movement in time are observed in the hypercube of the 40% H_2–air mixture. These spots are the images of the single cell in consecutive time points. The main feature of these spots is that emission spectra intensity dependences both on coordinate and on time have a maximum in the spots. The emission spectra of the spots are close to a gray body spectrum, that is the radiation of the spots (cells) really corresponds to emission of heated catalyst particles.

The ignition delay time (τ) is an important macrokinetic characteristic of chain thermal ignition, which can be measured in relatively simple ways. According to published data,[18,19] self-ignition in the shock tube and rapid compression machine is of kernel nature. The ignition of both hydrogen and *n*-pentane–air mixtures in a rapid mixture injection static reactor at 1 atm begins with the appearance of an initial center at the most chemically active site of the surface; thus, thermal ignition includes the stages of warming up, local ignition and flame propagation. Figure 3 presents the temperature dependence of ignition delay times for the 40% H_2–air mixture in the presence and absence of gas flow (Figure 2) over catalytic surface (Pt foil or Pt wire) assuming that the effective rate constant k is $\sim 1/\tau$.[6] The data were processed with the use of the Statistica 9 program package (Statsoft). As is evident from Figure 2, the effective activation energy E is the same for Pt foil or wire as well as for the presence or absence of gas flow. The experimental value of E is 19±3 kcal mol^{-1}, and it is close to that of a branching chain step of the hydrogen oxidation $H + O_2 \rightarrow OH + O$ (16.7 kcal mol^{-1}).[20] It means that the activated chain branching is the slowest step in the whole consequence of reactions leading to flame propagation.

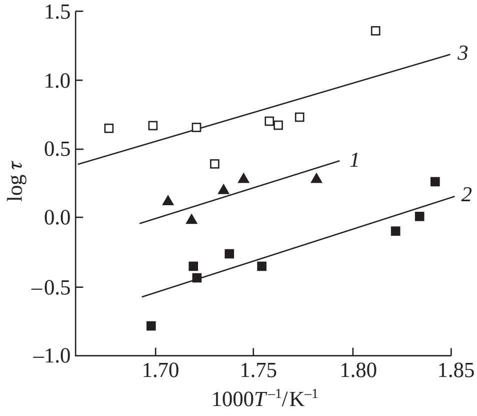

Figure 3 Temperature dependences of delay times of thermal ignition of the 40% H_2–air mixture in the presence and in the absence of a gas stream at P_0 = 1 atm: (*1*) the ignition initiated by a platinum foil, motionless gas, R = 0.987; (*2*) the ignition initiated by a platinum foil, circulating gas, R = = 0.989; (*3*) the ignition initiated by a platinum wire, motionless gas, R = 0.981.

As is well known,[21] the intercept of straight lines in Figure 3 is roughly the reciprocal of collision frequency. The surface area of Pt wire is less than that of Pt foil; therefore, the frequency of the encounters with the surfaces is less for Pt wire. The frequency of the encounters with the surfaces for Pt foil in motionless gas is less than that for the same foil in swirling gas.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.03.027.

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