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The features of ignition of hydrogen–methane and hydrogen–isobutene mixtures with oxygen over Rh and Pd at low pressures

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The experiments were performed with previously prepared stoichiometric gas mixtures $2H_2 + O_2$, $((20\div80\%)\ H_2 + (80\div20\%)\ \text{hydrocarbon})_{stoich} + O_2$. The reactor was quartz one 4 cm in diameter and 30 cm long heated up with an electric furnace (Figure S1); the temperature was controlled by a thermocouple. The reactor was supplied with an optical quartz window at its butt-end. The reactor was used for studying thermal/catalytic ignition provided by Pd wire (0.3 mm thick 80 mm long) and Pd foil (0.06 mm thick, 1 mm wide and 80 mm long) as well as Rh samples, which was made by electrochemical deposition of Rh layer 15 μm thick on Pd wire (0.3 mm thick 80 mm long). Pd was chosen because its coefficient of thermal expansion is the closest to that of Rh [12], since Rh wire is rather expensive.

The overall intensity of chemiluminescence was recorded with an FD–24 photodiode (Russia) sensitive in the range 450-900 nm. The recording of the experiment was performed with a Nikon 1J2 digital camera (Figure.S1). 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 was filled with the gas mixture from a high-pressure buffer volume to necessary pressure; the resistivity of the wires during ignition was measured. The pressure ignition limit was considered as a mean pressure P Torr, at P+0.03P the ignition occurs, at P-0.03P it does not occur, all other things being equal. The pump-down time between experiments was 30 min. The ignition limit was measured at increasing pressure with a step 2 Torr until the ignition occurred (a bottom-up approach, when increasing temperature from a state of no ignition).

The mean temperature of the wire during ignition was recorded by an ADC based acquisition system, taking into account the temperature dependence of metal electrical resistivity during computer analysis of the signal. The microstructures of carbon residues on noble metal surfaces were examined using field emission, ultra-high resolution scanning electron microscope Zeiss Ultra Plus (Germany) equipped with an X-ray Microanalysis console INCA

350, Oxford Instruments. Before each experiment, the reactor was pumped down to 10^{-2} Torr. Total pressure in the reactor was monitored with a vacuum gauge (Fig.S1a, 14), and the pressure in the buffer volume was monitored with a manometer. Chemically pure gases and 99.85% Pd were used.

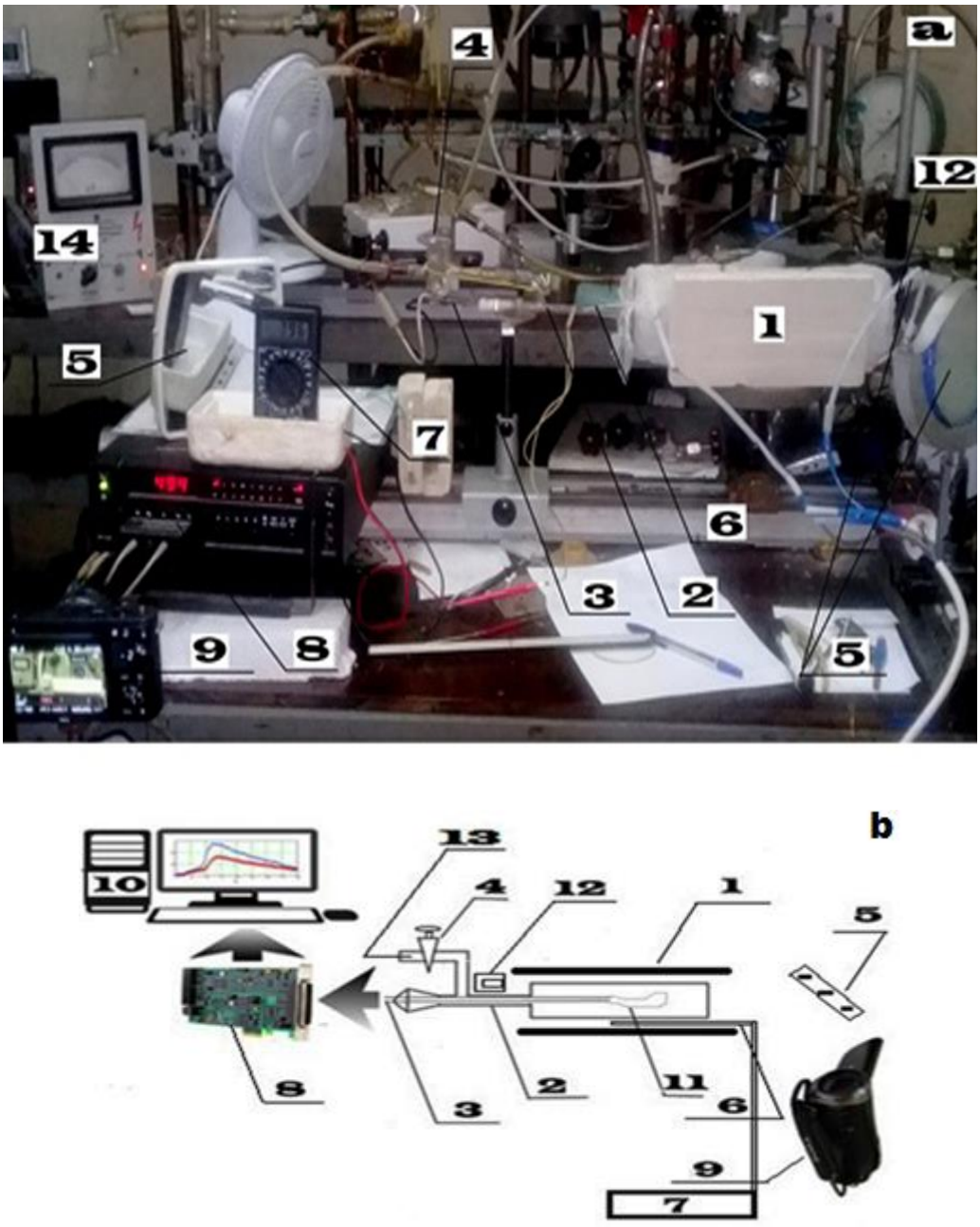

Figure S1 (*a*) Photograph and (*b*) schematic of the experimental installation for the study of thermal/catalytic ignition over noble metal wires. (*1*) electric furnace, (*2*) quartz reactor of 4 cm in diameter and 30 cm long, (*3*) vacuum feed-through, (*4*) vacuum valve, (*5*) rotating mirror, (*6*) thermocouple, (7) millivoltmeter for thermocouple, (*8*) ADC computer based system, (9) Nicon 1J2 digital camera, (10) computer, (11) noble metal wire, (12) FD-24a photodiode, (13) to pressure gauge, gas inlet, to the pump, (14) – pressure gauge.

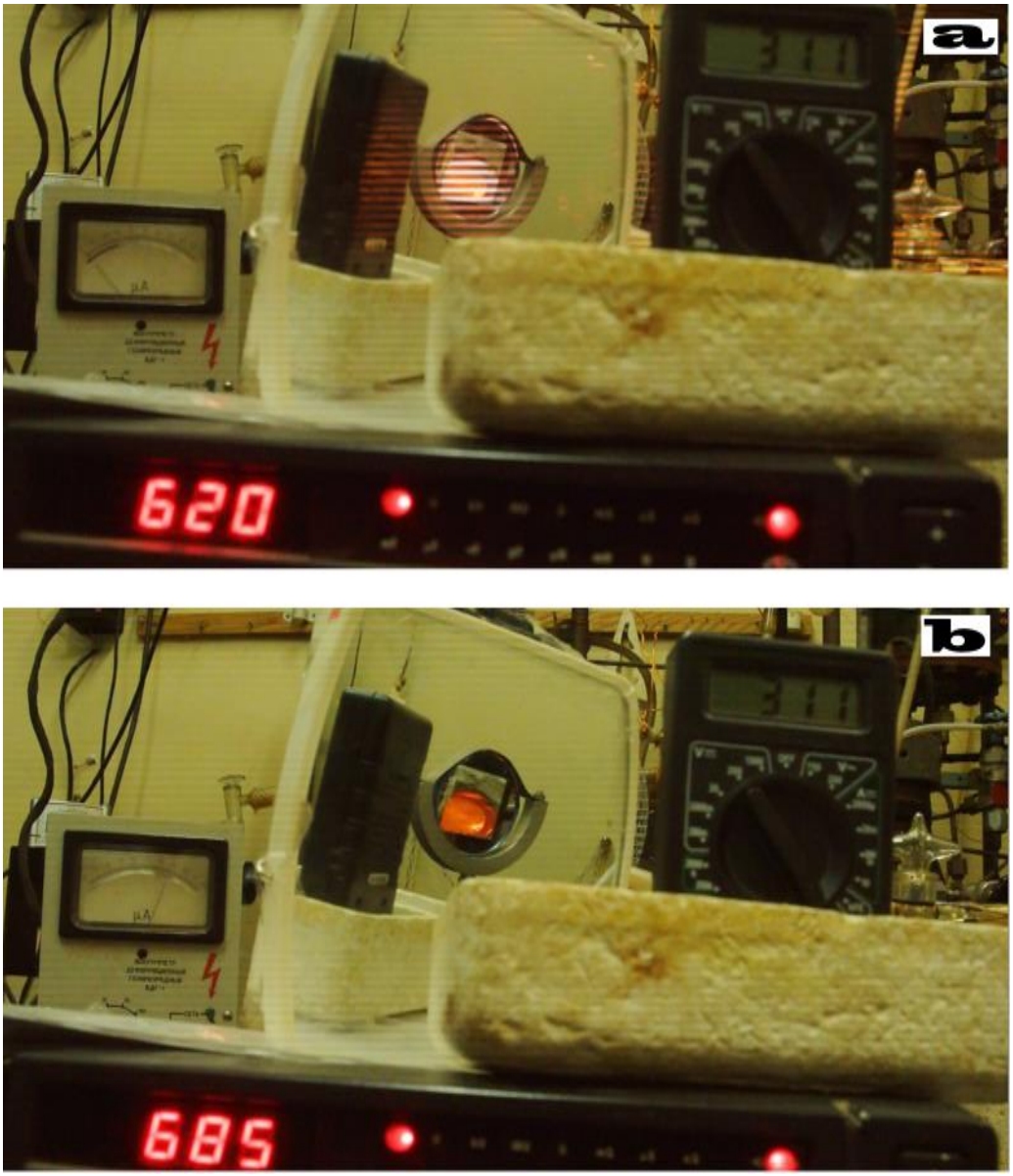

Figure S2 (*a*) The experiment (80% H_2 + 20% CH_4)$_{stoich}$ + O_2 above the ignition limit, Pd wire, 30 frames per second, 310 °C, 139 Torr (the pressure gauge is off, because the maximum of the gauge range is 100 Torr, the pressure was measured with mechanical vacuum gauge). (*b*) The experiment (80% H_2 + 20% CH_4)$_{stoich}$ + O_2 below the ignition limit, Pd wire, 30 frames per second, 310 °C, 70 Torr. The frames refer to the maximum intensity of light emission in the process. The figure in the bottom left is the current resistance of the wire, the figure at the top right is the temperature.