

## Surface modes of catalytic ignition of flammable gases over noble metals

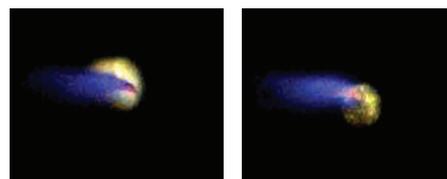
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The features of catalytic ignition of  $2\text{H}_2 + \text{O}_2$  and  $(70\% \text{H}_2 + 30\% \text{C}_2\text{H}_6)$  + air mixtures over Pd wire are established. It is shown that the catalytic wire or foil is heated unevenly before ignition: initial ignition centers always appear. With sequential ignitions, a clearly observed ignition center changes its location on the wire with every succeeding ignition.



High-speed filming (10 000 fps) of two consecutive catalytic ignition experiments

**Keywords:** surface, catalytic, ignition, hydrogen, hydrocarbon, oxidation, speed cinematography.

Safety requirements for hydrogen production, transportation and storage should be met before the widespread use of hydrogen as a fuel. Accidental ignition is one of the main concerns because hydrogen has much wider flammability limits than most conventional fuels.<sup>1</sup> A hot surface is one of the possible sources of ignition. Thus, it is important to be able to exclude the conditions under which ignition is possible when a mixture of hydrogen with an oxidizer hits a hot surface while entering the combustion chamber. However, hydrogen is difficult to ignite when compressed, and some ignition assistance is required, such as a glow plug.<sup>2</sup> Therefore, engine design requires an understanding of hot surface ignition.

Catalytic combustion of hydrogen is of interest because catalytic hydrogen combustion boilers operate at relatively low temperatures and can generate heat for household applications without  $\text{CO}_2$  and  $\text{NO}_x$  emissions.<sup>3</sup> Catalysts of  $\text{H}_2$  combustion reaction should possess oxygen storage capacity and thermal stability, ensuring that  $\text{H}_2$  oxidation would occur without explosion. These requirements can be met by using noble metals. In addition, knowledge of the reactions of  $\text{H}_2$  with  $\text{O}_2$  on the catalyst surface is necessary to understand the mechanisms of many commercialized processes, such as the preferential oxidation and combustion of  $\text{H}_2$ .

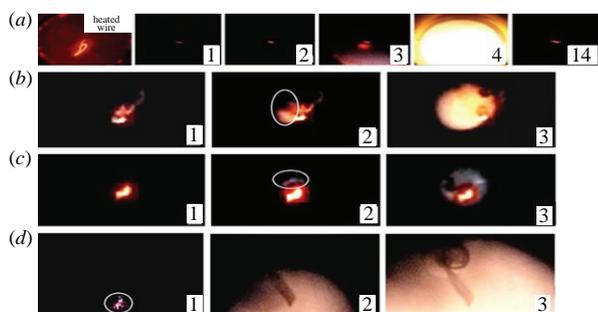
Noble metals are used as catalytic materials in catalytic converters, which serve as the main exhaust gas treatment system in motor vehicles and rely on redox processes to reduce toxic emissions. However, Pt-based catalysts are not effective enough with methane, while Pd catalysts can provide higher methane conversion.<sup>4</sup> Pd seems more advantageous for hydrogen recombiners in nuclear power plants because the ignition centers, which are catalytic particles formed during the decomposition of volatile oxide, do not appear in the gas phase, as they do when using a Pt catalyst.<sup>5</sup> The experimental value of the effective activation energy of the process is estimated by different methods as  $\sim 3.5 \pm 1.5 \text{ kcal mol}^{-1}$ , which is characteristic of surface processes.<sup>6</sup> It indicates a noticeable role of the dark reaction of  $\text{H}_2$  and  $\text{O}_2$  consumption observed directly at low pressures.<sup>6</sup> The occurrence of this reaction reduces the probability of an accidental explosion.

The interest in localized hydrogen generation, focusing on the hydrocarbon reforming process,<sup>7</sup> where methane is one of the prime sources, and Rh or Pt are the main catalysts of hydrocarbon to hydrogen conversion, has been renewed in the last decades.<sup>8</sup> Autothermal reforming as a method of hydrogen production has been gaining academic and practical interest due to its thermodynamically neutral nature and feasible operating conditions.<sup>9</sup> A number of experimental studies have been performed to investigate the ignition of hydrogen by a hot surface. Warnatz *et al.*<sup>10</sup> evaluated the catalytic combustion and ignition of hydrogen using detailed kinetic mechanisms for both surface and gas-phase reactions. Deutschmann *et al.*<sup>11</sup> studied catalytic ignition of different fuels on various catalytic materials. By numerical simulations, they proved that some reactants almost covered the surface before ignition. In a series of experiments with very thin catalytic wires, Rinnemo *et al.*<sup>12</sup> established the dependence of the critical ignition temperature of hydrogen mixtures mainly on their composition. Kalinchak *et al.*<sup>13</sup> analyzed catalytic ignition using a simplified model for heterogeneous chemistry. The results reveal the lack of universality of the ignition temperature concept and the need for a more profound understanding of the problem. Therefore, the peculiarities of  $\text{H}_2$  ignition over noble metals remain insufficiently clear.

In this work, experimental studies of the ignition of hydrogen and a hydrogen–ethane mixture over Pd wire and Pd foil at total pressures of 1–2 atm and initial temperatures of 60–270 °C were conducted to establish the peculiarities of ignition over the noble metal surface.<sup>†</sup>

Typical frame sequences in video recordings of catalytic ignitions at 1 atm of the 40%  $\text{H}_2$  + air mixture over Pd wire at 60 °C, the  $(70\% \text{H}_2 + 30\% \text{C}_2\text{H}_6)_{\text{stoich}}$  + air mixture over Pd wire

<sup>†</sup> The experiments were performed with stoichiometric gas mixtures  $(30\text{--}70\% \text{H}_2 + 70\text{--}30\% \text{C}_2\text{H}_6)_{\text{stoich}}$  + air and 40%  $\text{H}_2$  + air. The reactor was a heated stainless steel cylinder 25 cm long and 14 cm in diameter, equipped with removable covers and an optical sapphire window in one of them.<sup>14</sup> The evacuated and heated reactor was filled with a gas mixture from a high-pressure buffer volume up to 1 atm. Catalytic ignition was provided with



**Figure 1** High-speed filming of catalytic ignition of flammable gas mixtures over Pd surface under various initial conditions: (a) the 40%  $\text{H}_2$  + air mixture over Pd wire at 600 fps,  $T_0 = 60^\circ\text{C}$  and  $P_0 = 1$  atm (left frame: the appearance of the wire heated by an external source at 1 Torr); (b), (c) the  $(70\% \text{H}_2 + 30\% \text{C}_2\text{H}_6)_{\text{stoich}}$  + air mixture over Pd wire at 600 fps,  $T_0 = 61.5^\circ\text{C}$  and  $P_0 = 1$  atm (runs 1 and 2); (d) the 40%  $\text{H}_2$  + air mixture over Pd foil at 1200 fps,  $T_0 = 154^\circ\text{C}$  and  $P_0 = 1$  atm. White circles highlight primary ignition centers. The first frame corresponds to the moment of appearance of the primary ignition center.

at  $61.5^\circ\text{C}$  and the 40%  $\text{H}_2$  + air mixture over Pd foil at  $154^\circ\text{C}$  are shown in Figure 1.

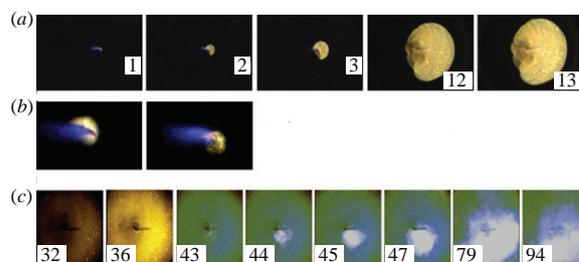
In accordance with published data,<sup>5,14</sup> Pd wire/foil becomes red-hot before and after ignition due to catalytic reactions on the Pd surface. The ignition temperature is lower for a  $(70\% \text{H}_2 + 30\% \text{C}_2\text{H}_6)_{\text{stoich}}$  + air mixture over Pd wire than for a more flammable 40%  $\text{H}_2$  + air mixture over Pd foil due to the higher rate of heat removal from the hot primary ignition center, determined by the section of the heat conductor, which is noticeably higher for the foil. Comparing frames 1–3 with the left frame in Figure 1(a), one can see that the wire is heated unevenly; localized initial centers of the ignition are clearly visible in the corresponding frames in Figure 1(b)–(d). As can be seen, the location of the primary ignition center changes with each subsequent ignition [Figure 1(b), (c), frame 2]. The result is consistent with that obtained earlier:<sup>5</sup> the gaseous process of ignition of  $\text{H}_2$ –air and hydrocarbon–air mixtures at atmospheric pressure begins with the appearance of an initial center at the most chemically active site of the surface.

All experiments on high-speed registration of catalytic ignition of the 40%  $\text{H}_2$  + air mixture over Pd foil using a Phantom camera (frame rate 4000 fps) have shown that the initial ignition center appears on the reactor surface after  $2.5 \times 10^{-4}$  s [Figure 2(a), frame 1]. In subsequent experiments under the same conditions, the location of the initial center changes [Figure 2(b)].

It should be noted that the high-speed filming of the developing catalytic ignition of the 40%  $\text{H}_2$  + air mixture over Pd foil (frame rate 10 000 fps) shows the movement of gas towards the center of the reactor after touching the reactor walls. It is noticeable by the movement towards the center of the dust particles detached from the walls [Figure 2(c), frames 32 and 36]. This event is followed by strong heating of the reaction products due to compression (the Mahe effect<sup>15</sup>).

This result means that the initiation of the thermal ignition process is always determined by the presence of reactive surface

Pd wire (0.3 mm thick and 80 mm long) or Pd foil (0.07 mm thick, 30 mm wide and 80 mm long, half rolled into a tube). The experiments on the detection of initial ignition centers on the catalytic wire using high-speed cinematography were carried out at a total pressure of 1 atm by means of a high-speed color camera Casio Exilim F1 Pro (frame rate 600 fps) and a high-speed PHANTOM camera (frame rate up to 10 000 fps) sensitive in the spectral range of 420–740 nm. The temperature measurement accuracy was  $\pm 0.3$  K. Before each experiment, the reactor was pumped down to  $10^{-2}$  Torr. The 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 and 99.85% Pd were used.



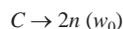
**Figure 2** High-speed filming of the catalytic ignition of the 40%  $\text{H}_2$  + air mixture over Pd foil at  $T_0 = 150^\circ\text{C}$  and  $P_0 = 1$  atm. (a) Frame 1 shows the moment of the appearance of the primary ignition center (frame rate 4000 fps). (b) Photographs of the initiation for two consecutive experiments (frame rate 10 000 fps). (c) Developing catalytic ignition (frame rate 10 000 fps). Frame 32 corresponds to the moment of the appearance of the primary ignition center.

centers. The properties of these centers are determined both by surface defects with excess free energy and by their catalytic properties. The ignition process includes warming up, local ignition and flame propagation stages. The chemical activity of different surface sites varies from one ignition to another. The basic feature of the ignition process is the occurrence of ignition at separate sites of the surface at a uniform temperature of the reactor surface. Therefore, combustion emerges on the reactor surface even under conditions of almost homogeneous warming up of a gas mixture.

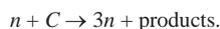
In this regard, it should be noted that the ignition of the combustible mixture in a heated reactor in a swirling flow, on the contrary, occurs homogeneously.<sup>16</sup> If there is no swirling flow in the installation, as is the case under the conditions of this work, then ignition occurs inhomogeneously, *i.e.*, the modes of thermal ignition are qualitatively different. These modes are obviously not determined by the reaction kinetics, which remains the same; in fact, they are controlled only by gas dynamics. This conclusion means that if the researcher uses, *e.g.*, a bypass method, then certain estimations of the flow geometry in the installation have to be made to exclude factors that should hinder obtaining the required results. The factors cannot be reduced to the comparison of characteristic times of homogeneous chemical and gas-dynamic processes; in this case, heterogeneous reactions must be considered.

It is important to note that there are some discrepancies in the analysis of the problem on autoignition of flammable gas mixtures with a catalytic wire. For instance, when determining the catalytic ignition temperature,<sup>11</sup> the flammable mixture slowly flowed around the catalytic wire at atmospheric pressure, or a stagnation flow was observed towards the catalytic foil. The temperature of the catalyst was increased by a stepwise increase in the current applied to the catalyst, *i.e.*, the catalyst was heated by an external source. However, the calculations of the autoignition temperature were compared<sup>17</sup> with the data on ignition from an external source,<sup>11</sup> which is incorrect. In addition, under flow conditions, the ignition temperature of  $\text{H}_2$ – $\text{O}_2$  mixtures over Pd foil decreases for leaner mixtures,<sup>11</sup> which agrees with the calculations.<sup>11,17</sup> On the contrary, under static conditions in a heated chemical reactor with a Pd wire inside, the autoignition temperature of the  $\text{H}_2$ – $\text{O}_2$  mixture increases with increasing  $\text{H}_2$  concentration.<sup>18</sup> Previously, the detailed mechanism of adsorption–desorption and surface oxidation of hydrogen on platinum is considered, and elementary constants of 23 elementary reactions are given.<sup>11</sup> Obviously, these are not experimental data but some estimates. Therefore, the reliability of the calculations is somewhat doubtful. In all the works considered above, a uniform temperature of the wire is assumed, which contradicts the experimental results presented here in Figures 1 and 2. These facts must be taken into account in further consideration.

We attempted to qualitatively include the above factors when considering ignition with a catalytically heated wire by numerical modeling using the compressible dimensionless reactive Navier–Stokes equations in the low Mach number approximation.<sup>5,19–21</sup> The reaction velocity in volume was presented by an elementary chain mechanism:



and



In this case, the simple Arrhenius equation<sup>5,6</sup> was replaced by equations (1)–(4):

$$\rho(C_t + vC_y + uC_x) = \Delta^2 C - \beta_0 n W, \quad (1)$$

$$\rho(n_t + vn_y + un_x) = \Delta^2 n + 2\beta_0 n W, \quad (2)$$

$$W = C \exp(\zeta - \zeta_1/T) \quad (\text{volume reaction}), \quad (3)$$

$$W_1 = C \exp(\zeta_1 - \zeta_1/T) \quad (\text{surface reaction}), \quad (4)$$

where  $\beta_0$  is the kinetic coefficient proportional to the Damköhler number.

The catalytic wire was simulated as a rectangular region in the middle of a rectangular reactor, as represented in Figure 3. Since the chemical exothermic branching reaction occurred at the boundaries of the region, the boundary conditions on the ‘wire’ took the following form:

$$T_t = \alpha \delta \beta_1 W_1 \quad (5)$$

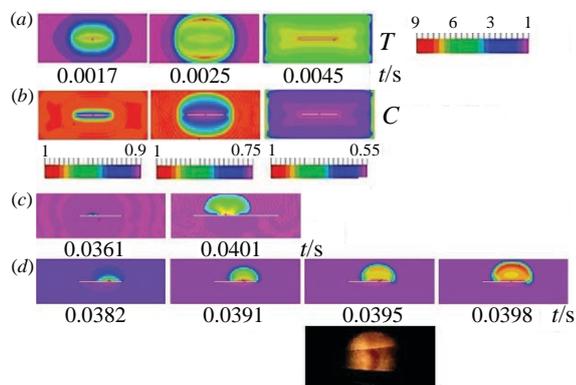
for heat release ( $\beta_1$  characterizes the heat release allocation for concentration,  $\alpha = 1$  for a homogeneous surface,  $\alpha = \sin 5x$  for an inhomogeneous surface, and  $\delta$  is a scale factor that determines only the duration of calculations),

$$n_t = \alpha \delta \beta W_1 \quad (6)$$

for surface branching and

$$C_t = 0.2C \quad (7)$$

for adsorption of the initial reagent. On the reactor walls, the parameters are  $n = 0$  (heterogeneous chain termination),  $u = 0$ ,  $v = 0$ ,  $\rho_x = 0$ ,  $C_x = 0$  and  $T_x = T_0$ , where  $x$  is the dimensionless coordinate. The parameters were taken equal to  $\zeta = 7.5$  (activation energy close to that of branching reactions in the volume oxidation of  $H_2$  and  $D_2$ ),  $\zeta_1 = 1.5$  (estimation of the activation energy of the surface process<sup>14</sup>),  $\beta = 0.15$ ,  $\beta_1 = 0.22$  and  $D_n = 0.9$



**Figure 3** Numerical simulation of ignition on a catalytic wire. (a) Change in the dimensionless temperature  $T$  for the dark reaction (see the scale on the right). (b) Change in the dimensionless concentration  $C$  for the dark reaction at  $T_0 = 1$  (see scales below). Change in the dimensionless temperature  $T$  for ignition at  $T_0 = 2$  and (c)  $\alpha = \sin 5x$  or (d)  $\alpha = 1$  (for other parameters, see the text). Bottom: photograph of a growing ignition center on Pt foil.

(diffusion coefficient). The initial gas temperature was set by the initial conditions:  $T_0 = 1$  for the dark reaction and  $T_0 = 2$  to ensure ignition.

The problem was solved by the finite element method using the FlexPDE 6.08 software package (PDE Solutions Inc., 1996–2008).<sup>22</sup> The calculation results (see Figure 3) take into account the main observed features of catalytic ignition. In a dark reaction, the rate of consumption of the initial reagent is less than during ignition. The appearance of local ignition centers on the catalytic wire in the case of ignition and the growth dynamics of the ignition center qualitatively agree with the experiment when comparing the experimental frame in Figure 2(a)<sup>5</sup> and calculated  $T$  at 0.0395 s [Figure 3(d)]. In addition, the calculation gives two primary ignition centers for an inhomogeneous surface, as in Figure 1(b) (frame 2). Thus, the qualitative model makes it possible to obtain both the mode of the emergence of primary ignition centers on the wire with subsequent local ignition and the mode of the dark catalytic reaction of the consumption of the initial reagent.

Based on the results obtained, it can be concluded that the heterogeneous chemical activity of various surface sites in reactors and converters using catalysts creates additional requirements for the optimal geometry of these devices.

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