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Catalytic activity of Pt and Pd in gaseous reactions of H_2 and CH_4 oxidation at low pressures

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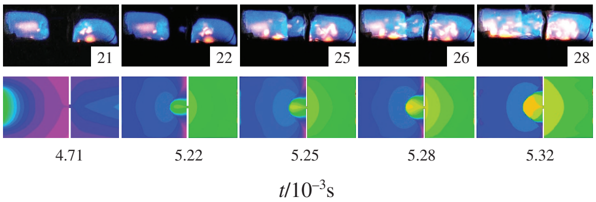
The value of effective activation energy of the dark reaction on Pd wire for $2H_2 + O_2$ reaction at 80 Torr has been estimated as 4.1 ± 1 kcal mol^{-1} that is characteristic of a surface process. It was demonstrated that at pressures up to 200 Torr, the rate of chain termination determines the critical diameter value in the flame penetration through Pt and Pd cylinders. The efficiency of Pd surface in the chain termination reaction was found much greater than that of Pt.



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In the history of nuclear power plants, the major failures include Three Mile Island (1979), Chernobyl (1986), and Fukushima (2011). The main reason for these disasters was the core–meltdown in a boiling water reactor (BWR).[1,2] At elevated temperatures (>1200 °C), reactor fuel cladding Zircaloy material (an alloy consisting of > 97% zirconium) generates H_2 gas *via* an oxidation reaction with the water steam.[3] The extensive quantities of H_2 and steam generated in the BWR system result in high pressure and temperatures, which may lead to the reactor failure. Thus, the removal of excessive amounts of H_2 is a crucial problem, and extensive research is required in order to overcome the highly undesirable phenomenon in nuclear industries. An improvement of passive catalytic hydrogen recombiners designed for the H_2 removal could reduce such risks.[4] Moreover, large-scale fuel cells are being developed for power generation in stationary, transportation and portable applications.[5] Often, fuel cells require an excessive amount of H_2 to achieve a stable voltage. The elimination of H_2 excess from the exhaust flow is required for their safe operation.[6] In addition, residential central heating can be accomplished by hydrogen or natural gas combustion boilers (HCB or NGCB). However, a direct H_2 combustion in NGCB causes NO_x emissions due to high operating temperatures. Catalytic hydrogen combustion boilers operate at relatively low temperatures and are capable of generating heat without unwanted CO_2 and NO_x emissions.[7] In the case of H_2 combustion reaction, the catalysts should possess properties such as oxygen storage capacity, thermal stability, and capability to oxidize H_2 without explosion. This can be achieved using noble metals that have a high adsorption capacity for H_2 and O_2 at low temperatures.[8] Moreover, understanding H_2 and O_2 behavior on the catalyst surface is important for clarifying the mechanisms of many commercialized processes such as preferential oxidation and H_2 combustion.

In catalytic combustors used in gas turbines, the fuel is burnt at more moderate temperatures to reduce NO_x emissions. However, Pt-based catalysts are not effective enough in the case of CH_4, which results in a small fraction of CH_4 contained in the exhaust gases under normal lean combustion operating conditions. Meantime, a Pd catalyst can provide a higher CH_4 conversion.[9]

For a thermal ignition of $2H_2 + O_2$ mixtures, it was found[10] that the catalytic activity of Pd surface is much higher than that over Pt foil at pressures up to 180 Torr over Pd foil at 288 °C. The activity of Pd foil manifests itself both in the occurrence of local ignition centers on the foil, from which combustion wave propagates, and in the dark catalytic reaction of the flammable mixture consumption. The experimental value of effective activation energy for the ignition process was estimated as 3.5 ± 1 kcal mol^{-1} that is characteristic of surface processes.[11]

The aim of the present work was to assess the activation energy of dark reaction (*i.e.*, the branched chain catalytic reaction of H_2 oxidation below the ignition limit). We have previously demonstrated[12] that Pd catalysts under certain conditions can suppress the developing flame propagation in a diluted CH_4–O_2 mixture due to the high efficiency of Pd surface in the reactions of termination of active combustion centers. Therefore, the kinetic factors can determine combustion regularities even under conditions of the high turbulence. This work was also aimed at an establishment of specific features of H_2 and CH_4 oxidation over Pt and Pd at low pressures (70–200 Torr).

A series of the experiments were performed with stoichiometric gas mixtures $2H_2 + O_2$.[†] The flame propagation in stoichiometric mixtures of CH_4 with O_2 diluted with CO_2 or Kr was investigated

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[†] A quartz reactor (4 cm diameter and 30 cm length) heated up with an electric furnace, whose temperature was controlled by a thermocouple,

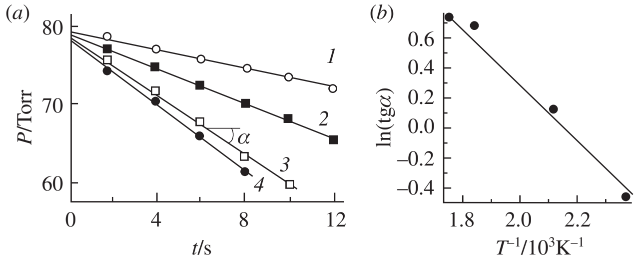

Figure 1 (*a*) Dependencies of total pressure in the $2H_2 + O_2$ mixture on time at (*1*) 150, (*2*) 200, (*3*) 270 and (*4*) 300 °C; and (*b*) Arrhenius plot for the dependencies shown in part (*a*).

at initial pressures of 100–200 Torr and 298 K in the pumped out horizontally located cylindrical quartz reactor.‡ To evaluate the temperature dependence for the dark reaction, the dependencies of total pressure of the $2H_2 + O_2$ mixture on time were experimentally determined [Figure 1(*a*)]. It should be noted that under the selected conditions, no dark reaction was observed in the presence of Pt wire instead of Pd. As one can see from Figure 1(*a*), the dependencies are straight lines. Figure 1(*b*) shows the dependence of the slope tangent of the lines in Arrhenius coordinates, which can be approximated by a straight line (the correlation coefficient is 0.982).§

The value of effective activation energy for the gross reaction can be estimated from Figure 1(*b*) as $E = 4.1 \pm 1$ kcal mol^{-1} that is characteristic of a surface process.[14] This value is close to that determined previously[11] for the dependence of H_2 fraction at the ignition limit over Pd surface in mixtures with O_2 on temperature in Arrhenius coordinates (3.5±1 kcal mol^{-1}). The activated ($E = 16.7$ kcal mol^{-1})[15,16] homogeneous branching step ($H^{\cdot} + O_2 \rightarrow O^{\cdot} + {}^{\cdot}OH$) is the slowest elementary reaction in the branching (*i.e.*, an increase in the number of active centers) cycle of reactions. Since the value of effective activation energy in the presence of Pd is considerably less, the branching cycle must change,[16] *e.g.*, at the expense of the additional branching step. The step can be $H^{\cdot} + HO_2^{\cdot} \rightarrow 2\,{}^{\cdot}OH$, wherein a relatively inactive $HO_2^{\cdot}$ turns into active ${}^{\cdot}OH$, *i.e.* extra branching occurs. It has been previously demonstrated[16] that accounting for that reaction allows one to explain an extension of the ignition area in the presence of external H atoms. Evidently, the verification of this assumption requires additional research.

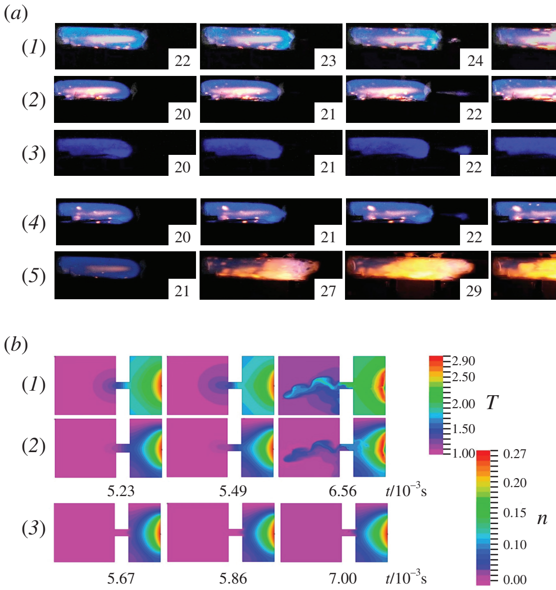

Figure 2 (*a*) High-speed filming of FF propagation through Pt cylinders (*1*) 25, (*2*) 20 and (*3*) 20 mm in diameter and filming through the interference filter (430 nm) for Pd cylinder (*4*) 25 and (*5*) 20 mm in diameter. Initial pressure was 170 Torr. The image on a frame corresponds to a frame number after the discharge. (*b*) Results of the calculation for the flame propagation through a single opening. Change in (*1*) dimensionless temperature, (*2*) active intermediate n for $n_x = 0$ (boundary conditions of type I) in the opening, and (*3*) active intermediate n for $n = 0$ (boundary conditions of type II). The scales of temperature T and dimensionless active intermediate n are shown on the right.

Figure 2 shows data from characteristic experiments on the high-speed filming of FF propagation in the combustible mixture at the initial pressure of 170 Torr through the Pt and Pd cylinders (length of 3 cm) inserted into a planar discus (diameter of 14 cm). As one can see, a laminar combustion occurs after the ignition. The ignition after obstacle does not occur in the immediate vicinity of obstacle, the first spot of ignition is observed at a certain distance from the obstacle surface [Figure 2(*a*), row *1*, frame 24 and Figure 2(*a*) rows *2*–*4*, frame 22], which is in agreement with our previous report.[13] When the flame passes the obstacle, one can observe a flame penetration through the obstacle in the case of Pt and Pd cylinders (diameter of 25 mm) as well as of the Pt cylinder (diameter of 20 mm) and a quenching effect at the smaller diameter (20 mm) of Pd cylinder, resulting in the extinction of a flame behind the orifice. It means that the critical diameter for a Pd cylinder is between 20 and 25 mm. The influence of obstacles can be expressed in a dual way. On the one hand, the flame interaction with an obstacle can cause the development of flame

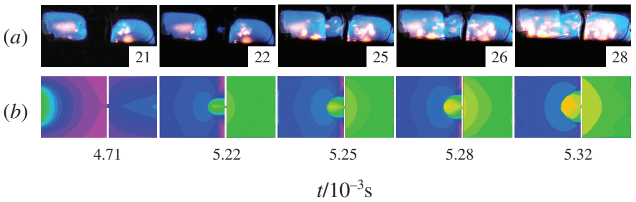

Figure 3 (*a*) High-speed filming of counter flame propagation through the Pd cylinder (diameter of 20 mm) and (*b*) results of the numerical modeling for the change in dimensionless temperature for $n = 0$ (boundary conditions for type II). Initial pressure was 180 Torr. The image in each frame corresponds to the frame number after discharge.

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was used. The reactor was supplied with a removable quartz window at its butt-end. The Pd or Pt wires (diameter of 0.3 mm and length of 150 mm) were placed in the reactor [Figure S1(*a*) in Online Supplementary Materials]. The pumped and heated reactor was filled with the gas mixture until the desired pressure. Before each experiment, the reactor was evacuated to 10^{-2} Torr. The total pressure in the reactor was monitored with a vacuum gauge with an indicator; its readings were recorded with a color digital camera Nikon 1.

‡ The reactor was 70 cm long and 14 cm in the diameter. The reactor with blunt ends was fixed in two stainless steel frames, supplied with inlets for gas injection and a safety shutter, which swung outward when the total pressure in the reactor exceeded 1 atm. The obstacle was a Pt or Pd cylinder (length of 40 mm) made of foil (thickness of 0.3 mm) and inserted into a vertical well-fitting planar discus (diameter of 14 cm) [Figure S1(*b*)]. Chemically pure gases, Pt (99.9%) and Pd (98.5%) were used. A pair of spark ignition electrodes was located near the left blunt end of the reactor.[13] The reactor was filled with the mixture up to the desired pressure. Then, a spark initiation was performed (the discharge energy was 1.5 J). Speed filming of the ignition dynamics and flame front (FF) propagation was performed from the reactor side[13] by color high-speed digital Casio Exilim F1 Pro cameras (frame frequency of 600 s^{-1}). The simultaneous detection of CH radicals (A1D–X2P) at 431 nm[13] was carried out using two high-speed movie cameras, one of them was equipped with a 430 nm interference filter. The video file was stored in computer memory, and its time-lapse processing was performed. The combustible mixture (15.4% CH_4 + 30.8% O_2 + 46% CO_2 + 7.8% Kr) was prepared prior to the experiment, wherein CO_2 was added in order to enhance the quality of filming by decreasing the flame propagation velocity, and Kr was added to diminish the discharge threshold.

§ The data were processed using the Statistica 9 software package (Statsoft).

instability, thus promoting its acceleration. On the other hand, the contact of flame with the obstacle surface may lead to an increased contribution of the heterogeneous reactions, in particular, a chain termination[16] as well as to an increase in heat losses. In our experiments, the obstacles differ in the material. The rate of dark reaction, even of fast H_2 oxidation on the Pd surface [see Figure 1(*b*)] was too small to attain a noticeable degree of conversion for the time interval of flame penetration through the cylinder [1/600 s, see Figure 2(*a*), *1–4*]. It means that the rate of chain termination determines the occurrence of the critical diameter. Thus, the efficiency of Pd surface in chain termination reaction is much greater than that of Pt.

It should be noted that under conditions of the counter flame (the initiated ignition was carried out simultaneously from both sides of the obstacle; in our experiment, at a different distance from the obstacle), the critical diameter gets markedly smaller: the flame penetrates through a Pd cylinder 20 mm in diameter [Figure 3(*a*)]. In this case, the boundaries of counter flame fronts interpenetrate each other, which means that gas dynamic factors are also important and consequently should be taken into account.

We have approximately estimated the contribution of chemical factors (chain termination on the noble metal surface) by numerical modeling based on compressible dimensionless reactive Navier–Stokes equations in a low Mach number approximation,[17] which describes the flame propagation in a two-dimensional channel. The equations revealed a qualitative consent with the experiments.[13] The problem was solved by a finite element analysis using the FlexPDE 6.08 software package[18] and the simple chain mechanism.[13] The initiation condition was taken as $T = 10$ on the right boundary of channel, and there was an orifice in the channel. Boundary conditions (including the orifice) were $C_\xi = 0$, $u = 0$, $v = 0$, $p_\xi = 0$, $n_\xi = 0$, and $n = 0$ only on the inner obstacle surface (this modeled the inner surface of cylinder made of noble metal) as well as a convective heat exchange according to $T_t = T - T_0$, where ξ is a dimensionless coordinate. The results of calculations revealed that the termination of active intermediate on the inner obstacle surface [$n = 0$, Figure 2(*b*), row *3* and Figure 3(*b*)] markedly affects the flame penetration, *viz.*, prevents the flame penetration through the opening in comparison with the case of $n_\xi = 0$ [see Figure 2(*b*), rows *1* and *2*]. Hence, regardless of the qualitative consideration, we managed to take into account the efficient action of active surface on the features of the flame penetration.

In conclusion, a Pd catalyst may suppress combustion under certain conditions as compared with that based on Pt and thereby demonstrates the effect opposite to a catalytic one due to the high efficiency of Pd surface in the chain termination reaction. Therefore, kinetic factors can be determining ones even under conditions of turbulence. The value of effective activation energy for the dark reaction on Pd surface was estimated as $E = 4.1 \pm 1$ kcal mol^{-1} that is characteristic of a surface process. This value is close to that determined for the dependence of H_2 fraction at the ignition limit on Pd surface for mixtures with O_2 on temperature. Under the reported conditions, no dark reaction on Pt wire was detected. It has been shown that the rate of chain termination determines the value of critical diameter for the flame penetration through Pt or Pd cylinders, while the efficiency of Pd surface in chain termination reaction is much greater than that of Pt.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.041.

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