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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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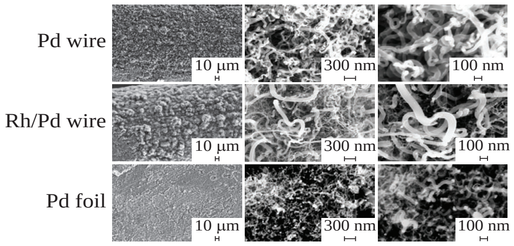
The flammability limits of stoichiometric mixtures (20–80% H_2 + 80–20% CH_4) + O_2 over Rh and Pd were determined in the pressure range 0–200 Torr and the temperature range 200–500 °C. It has been shown that the dark reaction in the mixture (80% H_2 + 20% C_4H_8)$_{stoich}$ + O_2 leads to the formation of carbon nanotubes with a mean diameter of 10–100 nm.

SEM micrographs of nanotubes



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As is well known, the reaction of methane with oxygen takes place in the dark on a hot platinum wire as a catalyst.[1] This reaction aroused great interest in the study of catalytic oxidation processes in connection with the prospect of industrial applications. In particular, these processes are promising for use in power generation systems,[2] to reduce methane concentrations in mines[3] and in vehicle emission control systems.[4] Hydrogen–hydrocarbon blends are attracting attention as alternative fuels for power generation for the following reasons. The first reason is related to the possibility of adding hydrogen to methane to improve performance and reduce pollutant emissions from lean combustion.[4] The second reason has to do with concerns about global warming, which can be mitigated by using hydrogen in both fuel cells and combustion devices.[5]

Palladium and other noble metals can also catalyze reactions during chemical vapor deposition to synthesize carbon nanostructures. Such nanostructures were synthesized on Pd nanoparticles supported on Al_2O_3.[6] The addition of hydrogen or oxygen to acetylene strongly affects the growth of products on Pd.[7] Various carbon nanostructures can be synthesized by catalytic chemical vapor deposition on Pd nanoparticles. With acetylene as a carbon precursor, multiwalled carbon nanotubes and carbon nanofibers were grown selectively, depending on temperature.[8]

Noble metals affect the flammability of hydrogen–methane mixtures in different ways. It was shown that the ignition temperature of the 40% H_2–air mixture over metallic Pd (70 °C, 1 atm) is ~200 °C lower than over a Pt surface (260 °C, 1 atm).[9,10] This difference indicates a prominent role of the dark reaction of H_2 and O_2 consumption observed directly at low pressures.[9] In addition, at temperatures below 320 °C, Pd ignites mixtures (30–60% H_2 + + 70–40% CH_4) + air (ϕ = 1), stoichiometric in terms of the amount of flammable gases[9] [equivalence ratio ϕ is a fraction of fuel in the mixture with air: $\phi H_2 + 0.5(O_2 + 3.76N_2)$], while metallic Pt cannot ignite these mixtures up to 450 °C, *i.e.*, Pd is more efficient than Pt. The experimental value of the effective activation energy of the process is estimated as 3.5 ± 1 kcal mol^{-1}, which is characteristic of surface processes.

It has been experimentally shown that the temperature limit of ignition of the mixtures (70% H_2 + 30% CH_4) + air (ϕ = 0.9, T = 317 °C) and (70% H_2 + 30% C_3H_8) + air (ϕ = 1, T = 106 °C) over Pd at P = 1.75 atm, measured with a bottom-up approach by temperature (when the temperature increases from a state of no ignition), drops noticeably after sequential ignitions to T = 270 °C for the H_2–CH_4 mixture and to T = 32 °C for the H_2–C_3H_8 mixture. The ignition limit returns to its initial value after the treatment of the reactor with O_2 or air, *i.e.*, a hysteresis phenomenon occurs. The ignition limits of the mixtures [70% H_2 + 30% (C_2, C_4, C_5 or C_6)] + air (ϕ = 0.6, 1.1, 1.2 or 1.2, respectively) over Pd are 25–35 °C at P = 1.75 atm, and there is no hysteresis effect. It has been found that the lean mixture (70% H_2 + 30% C_2H_6) + air (ϕ = 0.6) has the lowest temperature limit of ignition: 24 °C at 1 atm. The estimate of the effective activation energy for the ignition of mixtures over Pd is ~2.4 ± 1 kcal mol^{-1}, which is characteristic of a surface process.[11]

This work is devoted to experimental studies of low-pressure combustion of hydrogen–methane and hydrogen–isobutene mixtures over Rh and Pd surfaces at total pressures from 80 to 180 Torr and initial temperatures of 200–500 °C in order to establish the regularities of the temperature limits of flammability over noble metals and to determine the possibility of synthesizing carbon nanotubes from these gaseous precursors.

In the first part of the work, the thermal/catalytic ignition temperatures of $2H_2 + O_2$ and (20–80% H_2 + 80–20% hydrocarbon)$_{stoich}$ + O_2 mixtures over Pd and Rh/Pd were determined (Figure S1, see Online Supplementary Materials). Typical experiments with the (80% H_2 + 20% CH_4)$_{stoich}$ + O_2 mixture over Pd wire above and below the ignition limit are shown in

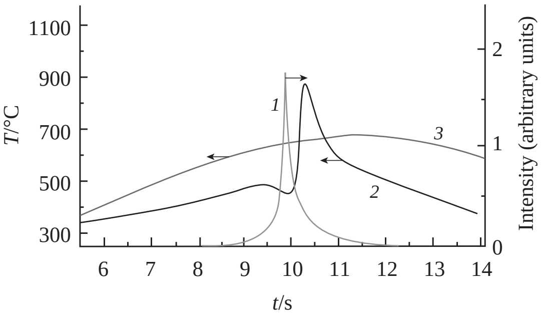

Figure 1 Measurements of chemiluminescence with a photodiode and warming-up according to the dependence of resistivity on temperature in the mixture (80% H_2 + 20% CH_4)$_{stoich}$ + O_2 over a Pd wire using an ADC computer-based data acquisition system: (*1*) ignition recorded using an FD-24a photodiode, T_0 = 310 °C, P_0 = 139 Torr; (*2*) mean temperature of the wire, T_0 = 233 °C, P_0 = 139 Torr, ignition occurred; (*3*) mean temperature of the wire, T_0 = 310 °C, P_0 = 70 Torr, no ignition.

Figures S2(*a*),(*b*). As is seen in Figure S2(*b*), the wire becomes red-hot even without ignition near the ignition limit, *i.e.*, a flameless ‘dark’ reaction of hydrocarbon consumption occurs.

The warming-up kinetics was monitored using the ADC computer-based data acquisition system by the temperature dependence of the resistivity of the Pd wire during combustion of the (80% H_2 + 20% CH_4)$_{stoich}$ + O_2 mixture (Figure 1). According to Figure 1, the activity of the catalytic wire is expressed both in the occurrence of an ignition transition from the surface into the reactor volume, and in a flameless ‘dark’ catalytic reaction of consumption of the flammable mixture. The catalytic preheating process provides warming-up sufficient to ignite the mixture at a given pressure (Figure 1, curve *2*). At lower pressure, even greater warming-up is not sufficient for ignition (Figure 1, curve *3*) since the mixture is far beyond the ignition region. Obviously, the warming-up value is underestimated because the wire is heated unevenly during ignition.[10]

The autoignition areas of $2H_2$ + O_2 mixtures over catalytic wires are presented in Figure 2 in *P*–*T* coordinates. Ignition occurs to the right of each curve, and no ignition occurs to the left. As shown in Figure 2, the Rh surface is the most active, and the Pd surface is the less active. Note that the hysteresis phenomenon for the ignition of the $2H_2$ + O_2 mixture is observed only over the Pd wire: namely, the ignition limit value measured with the wire, which is not treated with ignitions (a bottom-up approach, when the temperature increases from the state of no ignition) is higher than the value measured with a top-down approach. The same applies to the delay periods of ignition. The ignition limit is reversible: after the reactor has been treated with air or O_2, the limit returns to the value corresponding to the bottom-up approach when the temperature decreases from the state of autoignition.

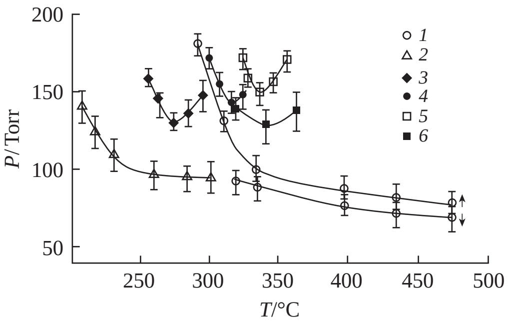

Figure 2 Autoignition areas of flammable mixtures over noble metal wires in pressure–temperature coordinates: $2H_2$ + O_2 over (*1*) Pd and (*2*) Rh/Pd; (*3*) (80% H_2 + 20% CH_4)$_{stoich}$ + O_2, (*4*) (60% H_2 + 40% CH_4)$_{stoich}$ + O_2 and (*5*) (50% H_2 + 50% CH_4)$_{stoich}$ + O_2 over Rh/Pd; (*6*) (80% H_2 + 20% CH_4)$_{stoich}$ + + O_2 over Pd. Ignition limits were measured in (↑) bottom-up and (↓) top-down approaches.

In the case of (H_2 + CH_4)$_{stoich}$ + O_2 mixtures, the ignition limit value measured over the Pd wire with the bottom-up approach is the lowest. Then, the ignition limit increases with each subsequent ignition until the autoignition area takes on a characteristic V-shape. The V-shape is probably defined by the following. With an increase in temperature, the value of the ignition limit first decreases due to an increase in the rate of the activated volume branching step or the cycle of elementary steps.[13] With a further increase in temperature, the rate of the dark surface reaction increases, resulting in an increase in the degree of fuel conversion. Thus, the fuel content in the mixture decreases and, therefore, the value of the ignition limit for a leaner mixture increases. In addition, only mixtures (80% H_2 + 20% CH_4)$_{stoich}$ + O_2, (60% H_2 + + 40% CH_4)$_{stoich}$ + O_2 and (50% H_2 + 50% CH_4)$_{stoich}$ + O_2 ignite over Rh/Pd wire, and only the mixture (80% H_2 + 20% CH_4)$_{stoich}$ + + O_2 ignites over Pd wire (or foil). Other mixtures are consumed only in the ‘dark’ reaction under the conditions of this work [see Figure S2(*b*)]. Note that there is no hysteresis phenomenon for ignition of the (H_2 + CH_4)$_{stoich}$ + O_2 mixture. For the ignition limit to return to its initial value, corresponding to the bottom-up approach, it is necessary to dissolve or mechanically remove the film deposited on the noble metal wire.

The second part of the work consisted in establishing the morphology of a film deposited on the noble metal surface using the (80% H_2 + 20% C_4H_8)$_{stoich}$ + O_2 mixture as the main precursor. A preliminary analysis of the formed film did not reveal any noticeable structures in the film deposited on the noble metal surface, both in the ignition mode (140 Torr) and in the ‘dark’ reaction mode (70 Torr) during combustion of a (H_2 + CH_4)$_{stoich}$ + + O_2 mixture. Therefore, the ‘dark’ reaction mode was chosen at 140 Torr in the (80% H_2 + 20% C_4H_8)$_{stoich}$ + O_2 mixture, which does not ignite under the conditions of this work. The results of the SEM investigation of the black residue formed in the reaction on the noble metal surface are shown in Figure 3. As can be seen, carbon nanotubes are formed in the ‘dark’ reaction mode.

After the Pd wire was first treated with two ignitions of the (80% H_2 + 20% CH_4)$_{stoich}$ + O_2 mixture and then subjected three times to a dark reaction with the (80% H_2 + 20% C_4H_8)$_{stoich}$ + O_2 mixture, carbon nanotubes were formed on the Pd surface, observed in SEM micrographs [Figure 3(*a*)]. Three times mean three operations to fill the reactor with the gas mixture (80% H_2 + 20% C_4H_8)$_{stoich}$ + O_2 up to 140 Torr for 15 s and pump it out. This sequence of operations leads to the formation of carbon nanotubes with a mean diameter of ~30 nm and a comparably

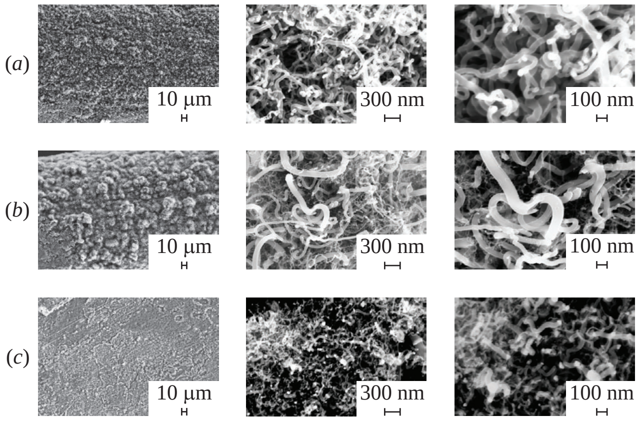

Figure 3 SEM micrographs of carbon nanotubes prepared on various substrates. (*a*) Pd wire was treated first with two ignitions of the (80% H_2 + + 20% CH_4)$_{stoich}$ + O_2 mixture and then three times with the (80% H_2 + + 20% C_4H_8)$_{stoich}$ + O_2 mixture at *P* = 140 Torr and *T* = 310 °C. (*b*) Rh/Pd wire or (*c*) Pd foil were treated three times with the (80% H_2 + 20% C_4H_8)$_{stoich}$ + + O_2 mixture at *P* = 140 Torr and *T* = 230 °C or *T* = 310 °C, respectively. Triple treatment consists of three times filling the reactor with a gas mixture up to 140 Torr for 15 s and pumping it out.

small variance. Figure 3(*b*) shows SEM micrographs of nanotubes formed on an Rh/Pd wire treated three times with the (80% H_2 + 20% C_4H_8)$_{stoich}$ + O_2 mixture. The wire was not treated by ignition of the (80% H_2 + 20% CH_4)$_{stoich}$ + O_2 mixture. As can be seen from the figure, nanotubes have more than one mean size. Nanotubes up to 100 nm in diameter can be seen, as well as nanotubes around 10 nm in diameter. Figure 3(*c*) displays SEM micrographs of nanotubes deposited on Pd foil treated three times with the (80% H_2 + 20% C_4H_8)$_{stoich}$ + O_2 mixture. These nanotubes have, in general, a mean diameter smaller than in cases (*a*) and (*b*); however, the variance in diameters seems to be rather high. Thus, process optimization requires further investigation.

In summary, it was shown that, at total pressures up to 200 Torr, the autoignition areas over the Rh and Pd surfaces are larger for $2H_2 + O_2$ mixtures than for (H_2 + CH_4)$_{stoich}$ + O_2 and (H_2 + + C_4H_8)$_{stoich}$ + O_2 mixtures; mixtures containing more than 50% hydrocarbons do not ignite. This behavior is directly related to the formation of a carbon-containing film on the noble metal surface. The fuel in the mixtures is consumed in a dark reaction. It has been shown that the dark reaction in the (80% H_2 + + 20% C_4H_8)$_{stoich}$ + O_2 mixture leads to the formation of carbon nanotubes with a mean diameter in the range of 10–100 nm.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.039.

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