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Ignition limits of hydrogen–methane–air mixtures over metallic Rh at a pressure of 1–2 atm

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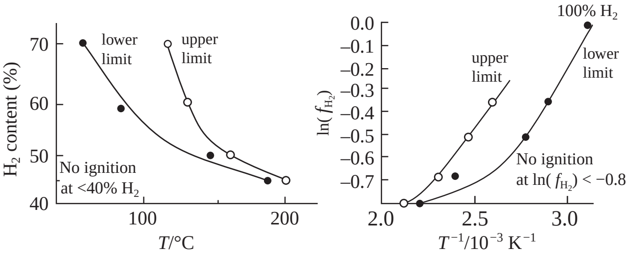
The ignition temperatures and effective activation energies of the ignition limits of mixtures (40–70% H_2 + 60–30% $CH_4)_{stoich}$ + air over Rh were experimentally determined at a pressure of 1 atm in the temperature range 20–300 °C. Over an ignition-treated Rh surface, the ignition temperature of a mixture of 70% H_2 + 30% methane + air is 62 °C. This indicates the potential of using Rh to markedly lower the ignition temperature of fuels based on hydrogen–methane mixtures.



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Hydrogen–hydrocarbon blended fuels are gaining attention as alternative fuels for energy production for two main reasons. The first reason is related to the increased efficiency of hydrogen–methane blended fuels, which results in improved performance of combustion devices, an increased range of their use and reduced pollutant emissions when using lean mixtures in stationary and mobile systems. The second reason is related to the development of hydrogen energy and the prospect of using H_2 in fuel cells and combustion devices.[1,2] With the commercialization of new hydrogen technologies, the problem of hydrogen safety becomes more and more urgent. Since the explosive concentrations of H_2 in a mixture with air range from 4% to 75% by volume, the transportation and storage of H_2 in a wide range of its concentrations is dangerous. It is known that with an increase in the methane content in a hydrogen–methane mixture, the upper concentration limit of combustion of such a mixture decreases markedly;[3] this makes the mixture much safer.[4] Natural gas and hydrogen can be mixed directly in the engine while the engine is running.[5] The hydrogen–methane mixture 'Hythane' was invented in the USA.[6] The number in the hythane marking means the energy share of hydrogen in the mixture: 5% in HY-5 for gasoline cars and 7% in HY-7 for diesel cars. The volume fraction of H_2 in the mixture can reach 20% and even 32%, as was the case in the Cummins–Westport gas engine. It has been theoretically and experimentally confirmed that the addition of hydrogen significantly increases the environmental safety and efficiency of the engine.[7]

The challenges in the safety of producing, transporting and storing hydrogen–hydrocarbon fuels need to be resolved before widespread use. One of the main problems is accidental ignition.[8] One possible source of ignition could be a hot surface. Therefore, it is imperative to be able to prevent the conditions under which ignition can occur when a flammable mixture is exposed to a hot surface. The catalytic combustion of pure hydrogen is of interest because boilers using this principle operate at relatively low temperatures and can produce domestic heat without CO_2 and NO_x emissions.[9] Combustion catalysts must have oxygen storage capacity and thermal stability; they must be able to ensure that fuel oxidation occurs without explosion. This can be achieved using noble metals.[10] Noble metals affect the flammability of hydrogen–methane blended mixtures in different ways. We experimentally found that Pd foil ignites mixtures (30–60% H_2 + 70–40% $CH_4)_{stoich}$ + air, whereas Pt foil cannot ignite them up to 450 °C. The estimated effective activation energy of the process is 3.5 ± 1 kcal mol^{-1}, which is characteristic of surface processes.[11] This indicates a noticeable role of the dark reaction of H_2 and O_2 consumption observed directly at low pressure.[11] It was also found that at 1.75 atm above the palladium surface, the ignition limit temperature of a mixture of 30% CH_4 + 70% H_2 + air ($\phi = 0.9$, $T = 317$ °C), measured by the bottom-up approach by temperature, decreases after subsequent ignitions and amounts to 270 °C. The ignition limit returns to its original value after the reactor is treated with oxygen or air, *i.e.*, a hysteresis effect is observed.[11] It was shown that during the combustion of hydrogen–propane–air mixtures ($\phi = 1$) over palladium at a total pressure of 1–2 atm, the ignition delay period τ first decreases with decreasing temperature, and then the value of τ increases until the ignition limit is reached; *i.e.*, there is a negative temperature coefficient (NTC) phenomenon.[11] It was shown that the NTC phenomenon is closely related to the state of the Pd surface.

This work is aimed at the experimental determination of ignition temperatures and effective ignition activation energies of mixtures (40–70% H_2 + 60–30% $CH_4)_{stoich}$ + air over Rh at a pressure of 1–2 atm in the temperature range of 20–300 °C under static conditions, to establish the catalytic efficiency of Rh as a promising igniter, to reveal the factors that determine the values of effective activation energies and to find out whether the NTC phenomenon exists during ignition.

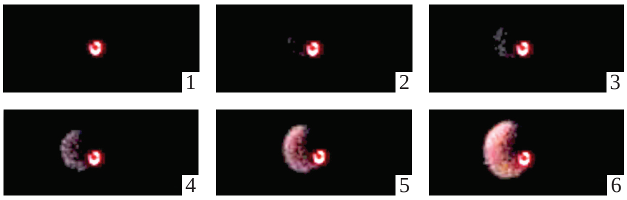

Figure 1 High-speed color filming of the initiation and propagation of a flame in a mixture of 70% H_2 + 30% CH_4 + air in the presence of Rh/Pd wire (1200 s^{-1}, $P_0 = 1.7$ atm, $T_0 = 71.1$ °C). The figures on each frame correspond to the sequence numbers of the video images during ignition.

All experiments on high-speed color filming (1200 s^{-1}) of catalytic ignition of hydrogen–methane–air mixtures over Rh/Pd wire showed that the initial ignition center appears on the wire surface[11] (Figure 1); in subsequent experiments under the same conditions, the place of origin of the initial center changes similarly to catalytic ignition over the Pd surface.[12] Thus, thermal ignition over a noble metal is determined by the reactions of adsorbed active centers on the surface, the behavior of which is determined both by surface defects with excess free energy and by the nature of the catalysts; ignition consists of the stages of warming-up, local ignition and flame propagation. The chemical activity of different areas of the surface varies from one ignition to another.

Time dependence of pressure during catalytically initiated ignition of a mixture of 45% H_2 + 55% CH_4 + air at $P_0 = 1.75$ atm over Rh/Pd wire at three temperatures (201, 189.8 and 181.4 °C) is shown in Figure 2.

The ‘upper’ ignition limit is measured by a bottom-up approach by temperature (at lower temperatures there is no ignition in a ‘fresh’ reactor, at higher temperatures ignition occurs).[15] When the ‘upper’ ignition limit is attained, further ignitions in the reactor, already treated with combustion, occur at lower temperatures, below the ‘upper’ limit, until the ‘lower’ ignition limit is reached (top-down approach). Thus, the ‘lower’ ignition limit refers to the surface of the catalyst (Rh) treated with ignitions; the ‘upper’ one corresponds to a ‘fresh’ reactor, in which there were no ignitions before.

Typical pressure *versus* time plots corresponding to successive temperatures below the ‘upper’ ignition limit are shown in Figure 2. As can be easily seen, the ignition delay period τ first decreases with decreasing temperature, but then the value of τ increases until the ‘lower’ temperature ignition limit is reached (at higher temperatures ignition occurs, at lower temperatures there is no ignition). Thus, we observe an NTC phenomenon similar to that described earlier.[11] The NTC phenomenon is caused by a change in the state of the Rh surface. As shown in previous work,[12] defects in the form of openings develop in samples treated with ignitions (Figure 5 in the cited paper[12]), and thus the surface area and the surface state change from one ignition to another.

To establish the boundaries of the region of catalytic ignition of H_2–CH_4 mixtures over Rh, the temperature dependences of the hydrogen concentration were experimentally determined both at the ‘upper’ and ‘lower’ ignition limits. The experimental dependences of the H_2 content in the mixture at 1.7 atm on the temperature at the ‘upper’ (curve *1*) and ‘lower’ (curve *2*) ignition limits of stoichiometric gas mixtures of H_2–methane–air over the Rh/Pd wire are presented in Figure 3(*a*).

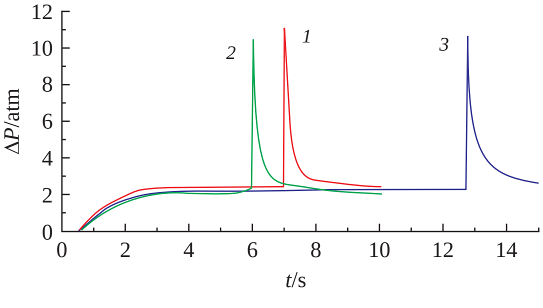

Figure 2 Pressure change during catalytic ignition of a mixture of 45% H_2 + + 55% CH_4 + air over Rh/Pd wire as a function of time at $P_0 = 1.75$ atm and (*1*) $T_0 = 201$ °C, (*2*) $T_0 = 189.8$ °C and (*3*) $T_0 = 181.4$ °C.

Figure 3(*a*) shows that in a reactor treated with ignitions, the ignition temperature of a mixture of 70% H_2 + 30% methane with air over the rhodium surface is 62 °C. For comparison, the ‘lower’ ignition limit of the same mixture over the palladium surface at 1.75 atm is 270 °C.[13] The result indicates the potential of using a rhodium catalyst to markedly lower the ignition temperature of fuels based on hydrogen–methane mixtures. In addition, the Rh catalyst is more stable in an $H_2 + O_2$ flame than Pd, Ru and Pt.[12] As can be seen from Figure 3(*a*), there is a critical condition for a volume reaction: a volume process occurs at 45% H_2, but it does not occur at $\leqslant$40% H_2. If the H_2 content is $\leqslant$40%, only a slow surface reaction takes place: the Rh/Pd wire remains bright red for several minutes. The nature of this critical phenomenon requires further investigation.

The dependences of the H_2 fraction in flammable mixtures on temperature in Arrhenius coordinates, as justified earlier,[11], are presented in Figure 3(*b*). As can be seen from the Figure, the dependences at $H_2 > 50\%$ can be approximated by straight lines (correlation coefficients > 0.98). The data were processed using the Statistica 9 software package (Statsoft). Figure 3(*b*) shows that the effective activation energies of both the upper and lower limits of H_2 + methane oxidation in the linearity range are approximately equal 2.5 ± 0.6 kcal mol^{-1}. This means that the key reactions responsible for the occurrence of the ‘upper’ and ‘lower’ ignition limits are almost certainly the same. Note that in order to ensure ignition, a set of reactions must occur in which chains develop (an increase or preservation[12] of the number of free valences).[11] Consequently, the activation energy of chain development should determine the temperature dependence of the overall process, as was observed for similar experiments with a Pt catalyst.[14] Thus, in case of the Rh/Pd catalyst, the chain development process is most likely heterogeneous, since the effective activation energy is <3 kcal mol^{-1}.

A feasible illustration of the occurrence of catalytic ignition limits was obtained in our recent work[15] by numerical simulation using compressible dimensionless reactive Navier–Stokes equations in the low Mach number approximation.[12,15–17] The reaction velocity in the volume was calculated for an elementary chain mechanism.[12,15] The chemical exothermic reaction of chain development occurred at the wire boundaries (rectangular area in the middle of the reactor). The Newmann boundary condition on the ‘wire’ for temperature took into account the heat release in the reaction of chain development; for the initial reagent and one active center, this accounted for the development of the surface chain and the adsorption of the initial reagent.[12] On the walls of the reactor, the Derichlet boundary condition hold true for the active center and

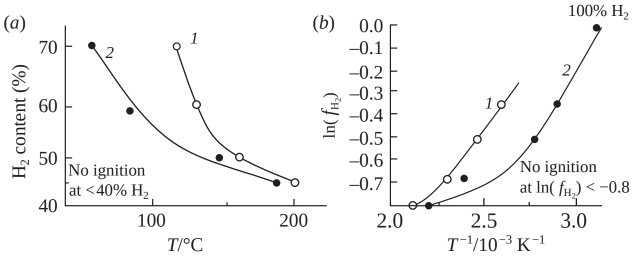

Figure 3 (*a*) Experimental temperature dependences of the H_2 content in the H_2–methane mixture at the (*1*) ‘upper’ and (*2*) ‘lower’ ignition limits of the H_2–methane–air mixture over the Rh/Pd wire at $P_0 = 1.7$ atm. (*b*) Arrhenius plots of the dependence of the logarithm of the H_2 fraction in the H_2–methane mixture at the (*1*) ‘upper’ and (*2*) ‘lower’ limits of the catalytic ignition of the H_2–methane–air mixture over the Rh/Pd wire on the reciprocal temperature.

velocity components; the Newmann boundary conditions were satisfied for the density, initial reagent and temperature. The initial gas temperature was set by the initial conditions: $T_0 = 1$ for dark reaction and $T_0 = 2$ to provide ignition.[12]

The model showed that in the dark reaction ($T_0 = 1$), the consumption rate of the initial reagent is slower than in ignition ($T_0 = 2$). Thus, it was possible to obtain both the mode of the emergence of primary ignition centers on the wire followed by local ignition, and the mode of the dark catalytic reaction of consumption of the initial reagent (Figure 8 in the cited article[12] and Figure 3 in the cited article[15]). The presence of the 'upper' and 'lower' limits of catalytic ignition can be interpreted according to the results of the cited work.[12] As the temperature rises and the Rh/Pd wire is treated with a hydrogen-containing gas mixture, an effective rhodium hydride catalyst forms on the surface of the wire. When the temperature corresponding to the 'upper' limit is attained, the mixture ignites over the rhodium hydride layer. Then, as the temperature decreases, the 'lower' limit of catalytic ignition is reached over the same layer of rhodium hydride. Then the fact that the activation energies of the 'upper' and 'lower' limits are very close to each other is due to the fact that ignition at both limits occurs over the same surface.

In summary, it was shown that in the reactor treated with ignitions, the ignition temperature of a mixture of 70% H_2 + 30% methane with air over the rhodium surface is 62 °C. The result indicates the potential of using a rhodium catalyst to markedly lower the ignition temperature of fuels based on hydrogen–methane mixtures. The critical condition of the volume reaction was revealed: the volume process occurs at 45% H_2, but is absent at $\leqslant$40% H_2. If the H_2 content is $\leqslant$40%, only a slow surface reaction occurs; this phenomenon is qualitatively described by our previous calculations. It was revealed that the effective activation energies of both the 'upper' and 'lower' limits of oxidation of the H_2 + methane mixture in the linearity range are approximately equal to 2.5 ± 0.6 kcal mol^{-1}; this means that the key reactions responsible for the occurrence of the 'upper' and 'lower' ignition limits are almost certainly the same. It was shown that for the Rh/Pd catalyst, the chain development process has most likely heterogeneous nature, since the effective activation energy is < 3 kcal mol^{-1}.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.06.043.

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