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Features of ignition of mixtures of hydrogen with hydrocarbons (C_2, C_3 and C_5) over rhodium and palladium at pressures of 1–2 atm

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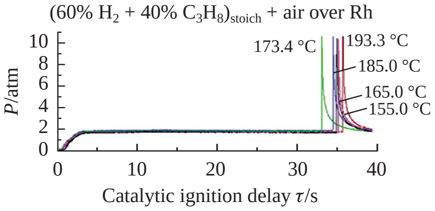
It was found that the reactivity of a hydrocarbon during oxidation catalyzed by a noble metal begins to play a significant role with an increase in the number of carbon atoms in its molecule. Thus, the process of hydrocarbon mass transfer to (or on) the catalyst surface determines the oxidation rate.



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For the widespread use of hydrogen as a fuel, it is first necessary to solve the safety problems of its production, transportation and storage. One of the main concerns is accidental ignition, since hydrogen has much wider flammability limits than most conventional fuels.[1] Thus, it is extremely important to be able to prevent conditions under which ignition may occur when a mixture of hydrogen and an oxidizer comes into contact with an active (hot, catalytic) surface. Catalytic combustion of hydrogen is of interest because boilers using this principle operate at relatively low temperatures and can generate domestic heat without CO_2 and NO_x emissions.[2] For an H_2 combustion reaction, catalysts must be thermally stable and ensure that H_2 oxidation occurs without explosion. This can be achieved using noble metals.[3]

Along with hydrogen, mixed hydrogen–hydrocarbon fuels and synthesis gas are of increasing interest as alternative fuels, since their combustion is a promising method of meeting the modern need to limit NO_x emissions in energy production, operation of internal combustion engines[4] and the production of target intermediate reagents for organic synthesis. The advancement in catalytically stabilized combustion technology requires the development of catalysts with improved activity (desired light-off temperature less than 450 °C), an understanding of catalytic surface processes, knowledge of the kinetics of low-temperature homogeneous reactions and its appropriate combination with the kinetics of heterogeneous reactions.[5] In the case of natural gas-fueled turbines, the concept of hydrogen-assisted catalytically stabilized combustion is of particular interest.[6] As is known, excess amounts of H_2 and steam generated in a boiling water nuclear reactor system create high pressure and temperature. This could lead to reactor failure. Therefore, removal of excess H_2 is necessary and extensive research is required to overcome this highly undesirable phenomenon in the nuclear industry. The use of noble metal catalysts for afterburning hydrogen in nuclear power plants is also of great interest.[7] However, even the oxidation of methane on noble metals has not been sufficiently studied,[8] and the nature of the surface processes is generally unknown.

The features of the catalytic ignition of mixtures of hydrogen with hydrocarbons and synthesis gas with air above the surface of metallic Rh are virtually not considered in contemporary literature. 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 at a pressure of 1 atm in the temperature range 20–300 °C were experimentally determined. Over the ignition-treated surface, the ignition temperature of the mixture (70% H_2 + + 30% methane) + air over Rh is 62 °C, which indicates the possibility of using Rh to noticeably reduce the ignition temperature of fuels based on hydrogen–methane mixtures.[9] The ignition temperatures and effective activation energies of ignition of a mixture 5–40% H_2 + air over Rh and mixtures [30–70% H_2 + 70–30% C_2H_6 (and C_2H_4)]$_{stoich}$ + air over Rh and Pd were experimentally determined at a pressure of 1 atm in the temperature range 20–300 °C. Rh metal has been shown to be more efficient than Pd, and the effective activation energies of ignition depend on the nature of both the catalyst and the hydrocarbon.[10] The ignition limits of stoichiometric mixtures (20–80% H_2 + 80–20% CH_4) + + O_2 over Rh and Pd were determined in the pressure and temperature ranges of 0–200 Torr and 200–500 °C, respectively.[11]

Similar data for Pd metal as a catalyst are also rather disparate. We have previously shown[11] that the effective activation energy *E* of the combustion process of mixtures (70–40% hydrogen + + 30–60% propane) + air over Pd at a total pressure of 1–2 atm is 2.2 ± 1 kcal mol^{-1}, which is typical for surface process.[13] It was found that in the sample treated with ignitions, defects appear in the form of openings focused on etching patterns.[12] This means that Pd is consumed in the chemical etching reaction caused by active combustion intermediates. It has been shown that before ignition, the catalytic wire is heated unevenly, with initial ignition centers appearing first. In addition, with successive ignitions, the primary ignition centers change their location on the wire from the first ignition to the next one.[12]

The effective activation energies of catalytic ignition of mixed fuels were determined taking into account the fact that it is hydrogen that provides catalytic ignition over a noble metal, which is confirmed by the fact that under our conditions catalytic ignition of pure hydrocarbons does not occur. Consequently, the following approximate dependence of the hydrogen content in the mixture

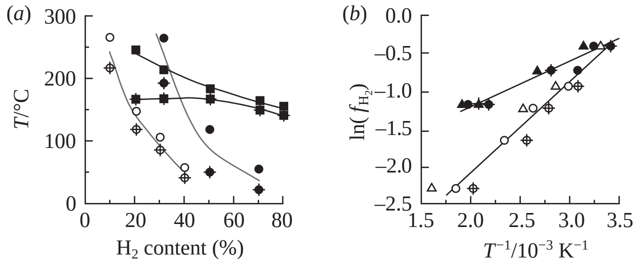

Figure 1 (*a*) Experimental dependences of the temperature (T) of the ‘upper’ and ‘lower’ limits of catalytic ignition on the H_2 content in the gas mixture for mixtures H_2 + ethane + air (●) and H_2 + ethylene + air (○) over the Pd wire and for the mixture $H_2 + CO$ (■) over the Rh/Pd wire ($P_0 = 1.7$ atm). (*b*) Arrhenius plots of the ‘upper’ and ‘lower’ catalytic ignition limits of the mixture H_2 + ethane + air over Pd (●) and Rh/Pd (▲), as well as the mixture H_2 + ethylene + air over Pd (○) and Rh/Pd (△). ‘Lower’ catalytic ignition limits are indicated by crosses on the symbols.

on the temperature of the catalytic ignition limit was assumed,[9] based on the following. For a stoichiometric mixture $2H_2 + O_2$, the ignition limit at low pressures is $2k_2[O_2]_{\text{lim}} = k_4$; *i.e.*, $[O_2]_{\text{lim}} = (1/2)[H_2]_{\text{lim}}$, and $[H_2]_{\text{lim}} = k_4/k_2$, then $[H_2]_{\text{lim}} = 2[O_2]_{\text{lim}} = k_4/k_2$, where k_4 is the rate constant of heterogeneous termination (weakly dependent on temperature) and k_2 is the branching rate constant.[1] From the latter equation we obtain the Arrhenius dependence of $\ln[H_2]_{\text{lim}}$ on $1/T$ with a positive slope.[1] The heterogeneous nature of the process in the presence of a noble metal significantly complicates the analysis. However, it can be shown that in the catalytic oxidation of H_2, the reaction rate depends mainly on the H_2 concentration, which for a steady state can be expressed as the ratio of some two effective constants.[13] Obviously, to understand the mechanism of the catalytic process, it is necessary to establish the features of the influence of hydrocarbons on the catalytic oxidation of mixed fuel.

The aim of this work is to identify the key features of catalytic ignition on metal rhodium and palladium in such mixed fuels as synthesis gas and hydrogen + hydrocarbon (ethane, ethylene, propane and pentane), namely, to establish the boundaries of the catalytic ignition regions, the dependence of effective ignition activation energies on the nature of the hydrocarbon and the role of dark oxidation processes.

Recall that the ‘upper’ limit of catalytic ignition is measured by a bottom-up approach in temperature (at lower temperatures there is no catalytic ignition over a ‘fresh’ noble metal wire, but at higher temperatures ignition occurs).[14] When the ‘upper’ catalytic ignition limit is attained, further ignitions over the already combustion-treated wire occur as the temperature drops below the ‘upper’ catalytic limit until the ‘lower’ catalytic ignition limit is attained (top-down approach). Thus, the ‘lower’ catalytic ignition limit refers to the catalyst (Rh) surface treated by ignitions, and the ‘upper’ one corresponds to a ‘fresh’ catalyst over which no ignitions have previously occurred.

Figure 1(*a*) shows the experimental dependences of the temperature of the ‘upper’ and ‘lower’ limits of catalytic ignition on the H_2 content in the gas mixture at $P_0 = 1.7$ atm for mixtures H_2 + ethane + air and H_2 + ethylene + air over the Pd wire and for a mixture of synthesis gas ($H_2 + CO$) with air over the Rh/Pd wire. The crosses on the symbols indicate the ‘lower’ catalytic ignition limits.

To identify the influence of the chemical nature of both the catalyst and the hydrocarbon on surface processes, Pd and Rh/Pd catalysts, as well as ethylene and ethane in mixtures with hydrogen, were used. The temperature dependences of hydrogen concentration at the limits of catalytic ignition were determined experimentally. Figure 1(*a*) shows that the mixture H_2 + ethylene + air ignites at lower temperatures than the mixture H_2 + ethane + air, *i.e.*, ethylene reacts more readily with active centers on the catalytic surface of palladium. The dependence of the H_2 fraction (f_{H_2}) in the flammable mixtures on temperature in Arrhenius coordinates, justified above (see also the recent article[9]), is presented in Figure 1(*b*). As can be seen from the figure, the dependence can be approximated by straight lines (correlation coefficients > 0.98). Data were processed using Statistica 9 software (Statsoft).

From the Arrhenius plots in Figure 1(*b*) it follows that the effective activation energy for the oxidation of H_2 + ethane is 1.25 ± 0.4 kcal mol^{-1} over both Pd and Rh/Pd wires. It is noticeably lower than the effective activation energy for the oxidation of H_2 + ethylene (2.8 ± 0.5 kcal mol^{-1}) over both Pd and Rh/Pd wires. Consequently, under the conditions of our experiments, the determining factor in catalytic ignition is not the chemical nature of the catalyst, but that of the C_2 hydrocarbon mixed with H_2.[15] However, to ensure ignition, a set of reactions must be implemented in which branching (an increase in the number of free valences) or chain propagation occurs.[1,12] The activated ($E = 16.7$ kcal mol^{-1}) homogeneous branching reaction $H + O_2 \rightarrow O + OH$ is the slowest step in the set.[1] Therefore, the activation energy of the branching should determine the temperature dependence of the overall process, as in similar experiments with Pt metal.[12] Thus, in the case of Pd and Rh/Pd, the branching (or chain propagation) reaction is most likely heterogeneous in nature, since the effective activation energy is < 3 kcal mol^{-1}.

It can be seen from Figure 1(*a*) that during the combustion of synthesis gas, both ‘upper’ and ‘lower’ limits of catalytic ignition over Rh/Pd are observed. In addition, Figure 1(*a*) demonstrates that the dependences of the catalytic ignition limits of synthesis gas over Rh/Pd are qualitatively different from the dependences for hydrogen–hydrocarbon fuel: the dependence of the ‘lower’ catalytic ignition limit has a distinct maximum, which indicates a more complex mechanism of the catalytic process for which it is impossible to implement the linear Arrhenius relation of $\ln(f_{H_2})_{\text{lim}}$ on $1/T$.

This means that the interpretation of the ‘upper’ and ‘lower’ catalytic ignition limits given in the previous work[12] should be clarified. Notice that, according to that work, when the temperature is increased and the Rh/Pd wire is treated with a hydrogen-containing gas mixture, an effective rhodium hydride catalyst is formed on the surface of the wire. When the temperature corresponding to the ‘upper’ catalytic limit is attained, the mixture ignites over a layer of rhodium hydride. Then, as the temperature decreases, the ‘lower’ limit of catalytic ignition is reached over the same layer of rhodium hydride. Consequently, the activation energies of the ‘upper’ and ‘lower’ catalytic limits are very close to each other, since ignition at both limits occurs over the same surface. For synthesis gas, CO poisoning of rhodium oxide must be taken into account.

Figure 2(*a*) shows the experimental dependences of the temperature of the ‘upper’ and ‘lower’ limits of catalytic ignition on the H_2 content in the gas mixture at $P_0 = 1.7$ atm for the

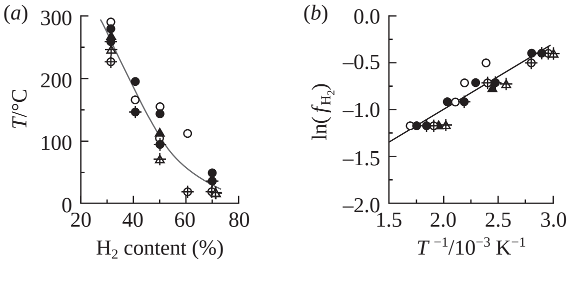

Figure 2 (*a*) Experimental dependences of the temperature (T) of the ‘upper’ and ‘lower’ limits of catalytic ignition on the H_2 content in the gas mixture and (*b*) Arrhenius plots of these limits for the mixture H_2 + propane + air over Pd (○) and Rh/Pd (●) wires, as well as for the mixture H_2 + *n*-pentane + air (▲ and △) over the Rh/Pd wire ($P_0 = 1.7$ atm). The crosses on the symbols indicate the ‘lower’ catalytic ignition limits.

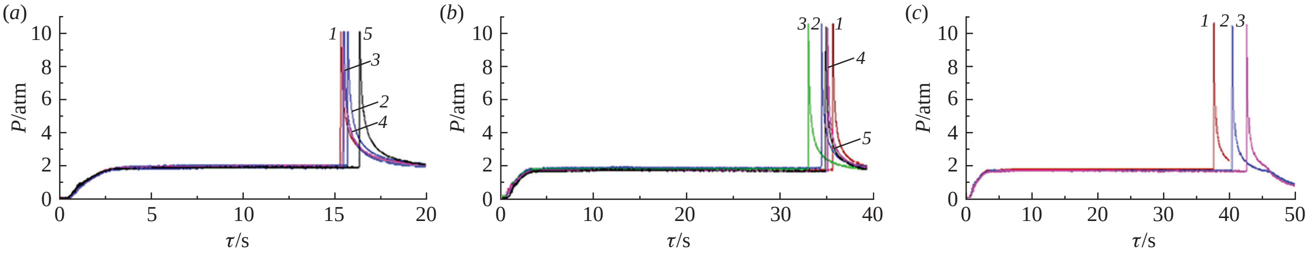

Figure 3 Delay periods (τ) for catalytic ignition of hydrogen–propane and hydrogen–pentane mixtures over Rh: (*a*) (50% H_2 + 50% $C_3H_8)_{stoich}$ + air at temperatures (*1*) 129.5, (*2*) 125, (*3*) 117.1, (*4*) 111 and (*5*) 101 °C; (*b*) (60% H_2 + 40% $C_3H_8)_{stoich}$ + air at temperatures (*1*) 193.3, (*2*) 185, (*3*) 173.4, (*4*) 165 and (*5*) 155 °C; (*c*) (50% H_2 + 50% $C_5H_{12})_{stoich}$ + air at temperatures (*1*) 94.5, (*2*) 79.7 and (*3*) 70.1 °C.

mixture H_2 + propane + air over Pd and Rh/Pd wires, as well as for the mixture H_2 + *n*-pentane + air over the Rh/Pd wire.

As can be seen in Figure 2(*b*), the effective activation energy value derived from the Arrhenius dependence of the logarithm of H_2 content on the reciprocal temperature at both the ‘upper’ and ‘lower’ limits over both Pd and Rh/Pd for all mixtures is 1.2 ± 0.3 kcal mol^{-1}. Thus, for a mixture of H_2 + $C_3(C_5)$-hydrocarbon, the effective activation energy of both limits does not depend on the chemical nature of either the hydrocarbon in the mixture or the catalyst.

It was found that the values of the delay periods of the catalytic ignition of hydrogen–propane mixtures weakly depend on the initial temperature (Figure 3).

This means that the delay period in combustible mixtures can be understood as the sum of at least two terms. One of them is temperature dependent and is determined by the proximity of the mixture to the catalytic ignition limit (true delay period). The second depends weakly on temperature and is significantly larger than the first. The second process, weakly dependent on temperature, may be the mass transfer of one of the reactants to the surface of the catalyst. Such relatively long delay periods of catalytic ignition and their independence from the initial temperature allows us to conclude that the catalytic ignition of hydrogen–propane (*n*-pentane) mixtures is determined, *e.g.*, by the diffusion of hydrocarbon to the surface of the catalytic wire either from the bulk or on the surface to some active center.

In summary, it was shown that under the conditions of our experiments, the determining factor in the kinetics of catalytic ignition is not only the chemical nature of the catalyst, but also the chemical nature of the C_2 hydrocarbon in a mixture with H_2. The limits of catalytic ignition of synthesis gas over Rh are qualitatively different from those for combustible hydrogen–hydrocarbon mixtures: the dependence of the ‘lower’ catalytic limit on temperature has a distinct maximum, which indicates that the mechanism of the catalytic process is more complex than that for hydrogen–methane mixtures, and the Arrhenius dependence of $\ln(f_{H_2})_{lim}$ on $1/T$ could not be applied. Therefore, it is necessary to clarify the interpretation of the ‘upper’ and ‘lower’ limits of catalytic ignition given in the literature. The relatively long delay periods for the catalytic ignition of hydrogen–*n*-pentane mixtures (tens of seconds) and the absence of dependence of the delay periods on the initial temperature allow us to conclude that the catalytic ignition of hydrogen–propane/*n*-pentane mixtures is determined mainly by the diffusion of the hydrocarbon to the surface of the catalytic wire. Thus, during the oxidation of mixtures of hydrogen and ‘short’ hydrocarbons, the main factor determining catalytic ignition is the hydrogen oxidation reaction on the catalytic surface. With an increase in the number of carbon atoms in a hydrocarbon, factors related to the chemical structure, that is, the reactivity of the hydrocarbon during catalytic oxidation, begin to play a significant role; and then the oxidation rate is already determined by the processes of hydrocarbon diffusion to (or on) the catalyst surface.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.01.042.

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