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Influence of Thermal Diffusion on the Hysteresis Area of Hydrogen Impurities' Catalytic Combustion on Platinum Wire

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A complex investigation of the hysteresis mechanisms of heat and mass exchange and catalytic flameless combustion of hydrogen-air mixtures on platinum's particles and wires. Thermal diffusion of hydrogen does not affect the critical conditions for self-ignition mixture unlike conditions extinction mixture. Method is proposed the analytical determination of the hysteresis areas heat and mass exchange particles (wires) catalyst. Inside the areas there is a catalytic ignition, and outside - stationary states of oxidation and catalytic combustion of combustible gas in the air.

Keywords: metal oxidation catalysts, wire, hydrogen, hysteresis heat and mass exchange, self-ignition, extinction, shallow (flameless) burning.

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The basis of thermochemical gas analyzers for small impurities of combustible gases in the air-gas mixture is in using dependence on the speed of chemical heat generation or temperature of particle (wire) catalyst from concentration of impurities [1-5]. With their catalytic flameless combustion catalyst temperature increase can be linearly. We proved that this is possible with the small heat loss by radiation, the first order of catalytic reactions in combustible gas and its flow in the thermodiffusion mode. The criterion of radiation heat exchange from the cold walls of reaction device as dimensionless diameter [4], which is less temperature dependence of wire (particle) catalyst, depends linearly on the impurity concentration of flammable gas that is necessary for selection of operating modes for thermochemical gas analyzer.

The aim of this work was to study the effect of diffusion-kinetic ratio (Semenov criterion), thermal diffusion on hysteresis characteristics and heat and mass exchange to the degeneration for the catalytic combustion of hydrogen small impurities on platinum wires (particles) according to gross reactions $H_2 + 0.5O_2 = H_2O$. For this reaction is typical Lewis criterion value Le ≈ 3 and essential role thermal diffusion [6, 7].

This reaction is first order to the concentration of hydrogen [6]. Speed of heterogeneous-catalytic reaction W_a (kg / (m^{2}s)) for small impurities of hydrogen proportional mass fraction (relative concentration) near the surface of the catalyst $Y_{a,s}$:

$$W_a = k\rho_{gs}Y_{a,s}\,,\quad k = k_0 \exp\left(-\frac{E}{RT}\right), \qquad (1)$$

where ρ_{gs} – density near the surface of the mixture, kg / m^3; k , k_0 – constant of chemical reactions and pre-eksponent, m/s; E – activation energy, J/mol; R – universal gas constant, J/(mol·K), T – catalyst temperature, K.

To establish the surface concentration of hydrogen let present density of hydrogen mass flow j_a to unit of catalyst surface under the Fick law with regard to thermal diffusion in the form:

$$-j_a = -D_a\rho_g\left(\frac{\partial Y_a}{\partial r} + \frac{k_T}{T_g}\frac{\partial T_g}{\partial r}\right)\Bigg|_{r=r_s} \quad \text{or}$$

$$-j_a = -D_a\rho_g\left(\frac{\partial Y_a}{\partial r} + k_T\frac{\partial \ln T_g}{\partial r}\right)\Bigg|_{r=r_s}.$$

Here $k_T = D_T/D_a$ – the ratio of thermal diffusion coefficient D_T and concentration diffusion D_a; T_g – gas mixture temperature at a distance r from the particle; ρ_g – density of the gas mixture, r_s – catalyst radius.

According to the present model of film on the surface of the wire can used the equation for c-coefficients of mass exchange and heat exchange

$$D_a \rho_g \left.\frac{\partial Y_a}{\partial r}\right|_{r=r_s} = \frac{D_a Sh}{d} \rho_g \left(Y_{a,\infty} - Y_{a,s}\right)$$

and $$-\lambda_g \left.\frac{\partial T_g}{\partial r}\right|_{r=r_s} = \frac{\lambda_g Nu}{d}\left(T_{g,s} - T_{g,\infty}\right),$$

Here $T_{g,\infty}$ and $Y_{a,\infty}$ – are the gas mixture temperature and mass fraction of hydrogen away from the particles; $T_{g,s} = T$ – is gas mixture temperature near the particle surface.

Sherwood and Nusselt numbers *Sh* and *Nu* for catalyst blown by gas mixture can be determined by empirical dependences

$$Nu = A\mathrm{Re}^x \mathrm{Pr}^m, \quad Sh = A\mathrm{Re}^x Sc^m,$$

allowing you to link them $Nu = Sh \cdot \left(\mathrm{Pr}/Sc\right)^m = Sh \cdot Le^m$, where $Le = D_a / a_g$ – Lewis criterion, Pr – Prandtl number, S*c* – Schmidt number, Re – Reynold's number.

Accordingly, between the coefficients of mass transfer β and heat transfer α there is a connection

$$\alpha = c_{pg}\rho_g \beta Le^{-1+m}, \ \alpha = \frac{\lambda_g Nu}{d}, \ \beta = \frac{D_a Sh}{d}.$$

Here c_{pg} – air specific of the heat at constant pressure, λ_g – air thermal conductivity, *d* – diameter of platinum wire.

Thus the density of mass flow of hydrogen near the surface of the catalyst is:

$$j_a = \beta\rho_g \left(\left(Y_{a,\infty} - Y_{a,s}\right) + \frac{k_T}{T}\left(T - T_{g,\infty}\right) \cdot Le^m \right), \quad (2)$$

Thermal diffusion coefficient k_T proportional to the concentration of hydrogen and can be calculated by the approximate formula [8]:

$$k_T = \frac{D_T}{D_a} = \left(2-n\right)\ Y_{a,\infty},$$

where *n* – is index in the temperature dependence of the concentration diffusion coefficient.

From equality of chemical reactions speed (1) and the density of the mass flow (2) get surface concentration of hydrogen including thermal diffusion

$$Y_{a,s} = Y_{a,\infty}\frac{1+\psi_T}{1+Se},$$

$$Se = \frac{k \cdot \rho_{gs}}{\beta \cdot \rho_g}, \ \psi_T = \left(2-n\right)\frac{T - T_{g,\infty}}{T} Le^m.$$

where *Se* – diffusion-kinetic relation, ψ_T - amendment to thermal diffusion.

To analyze the stationary states (lasting and critical) for catalyst temperature can be used combustible gas concentration dependence of stationary temperature catalyst. Using it to analyze the impact of the gas temperature T_g and diameter d to the values of concentration $Y_{a,\infty}$, that lead to stable catalytic combustion conditions and critical concentrations ignition $Y_{a,i}$ and extinction $Y_{a,e}$. With equality between speed of chemical heat generation and heat emission(temperature stationary condition of the catalyst) [6]:

$$Q_a k \rho_{gs} Y_{a,\infty} \frac{1+\psi_T}{1+Se} = c_{pg}\rho_g \beta Le^{-1+m}(T - T_{g,\infty}), \quad (3)$$

dependence of concentration of combustible gas from catalyst stationary temperature (fig.1) represented as:

$$Y_{a,\infty} = \frac{Sh}{d}\frac{D_a \rho_g}{\left(1 + A_T \dfrac{T - T_{g,\infty}}{T_Q}\right)\rho_{gs} k_0}\left(1+Se\right)\frac{\left(T - T_{g,\infty}\right)}{T_Q}\exp\left(\frac{E}{RT}\right), \quad (4)$$

$$\psi_T = A_T \frac{T - T_{g,\infty}}{T_Q}, \ A_T = \left(2-n\right)\frac{T_Q}{T} Le^m, \ T_Q = \frac{Q_a Le^{1-m}}{c_{pg}},$$

Here Q_a - the heat of reaction for 1 kg of combustible gas.

Thermal properties of the gas mixture in the presence of small impurities of hydrogen almost do not differ from the properties of air. In this work they are calculated in the arithmetic average temperature T_* between the temperature of the catalyst and gas mixture temperature (410 K in the catalytic oxidation of hydrogen) [5]:

$$\rho_g = \rho_{g0}\frac{2T_0}{T + T_{g,\infty}}, \ \rho_{gs} = \rho_{g0}\frac{T_0}{T},$$

$$D_a = D_{a0}\left(\frac{T + T_{g,\infty}}{2T_0}\right)^n,$$

$$c_{pg} = c_{pg0} + \gamma\left(\frac{T + T_{g,\infty}}{2} - T_0\right).$$

Calculations were performed with the following parameters' values: platinum filament diameter 100 mcm, *E* = 55 kJ/mol, $k_0 = 0.8 \cdot 10^6$ m/s, Q_a = 120.9 MJ/kgH$_2$, $D_{a0} = 0.6 \cdot 10^{-4}$ m^2/s, *m* = 0.33, *n* = 1.75, *Sh* =

0.51, T_0 = 293 K, λ_{g0} = 0.024 W/(m·K) = 1.293 kg/m^3 = 1005 J/(kg·K).

On stationary dependence $Y_{a,\infty}(T)$ maximum (fig. 1) describes critical condition catalytic self-ignition (point **i**), and the minimum - critical extinction condition (point e) [3]. In low temperature oxidation mode catalyst temperature slowly increases with the concentration of fuel. When the temperature reaches T_i happens abrupt change of regime to sustainable mode of catalytic gas combustion on the surface of the wires catalyst. Temperature of catalytic combustion also increases with increasing of $Y_{a,\infty}$. Conversely, a decrease of $Y_{a,\infty}$ catalytic combustion temperature decreases and when reaching critical values Y_{ae} i T_e occurs extinction of catalytic chemical reaction. The curve that lies between the points **i** and **e**, determines ignition temperature of the reaction by heating the catalyst.

To analyze the stationary states (sustainable and critical) catalyst temperature can be used in temperature dependence of the air-gas mixture from a stationary temperature of wire (particle) catalyst (fig. 2). Let present condition of stationary (1) in form:

$$(T - T_{g,\infty})c_{pg}\rho_g \beta Le^{-1+m}\left(\frac{k}{\beta}\frac{\rho_{gs}}{\rho_g} + 1\right) = Q_a k \rho_{gs} Y_{a,\infty}\left(1 + A_T\frac{\left(T - T_{g,\infty}\right)}{T_Q}\right), \tag{5}$$

Thus we can obtain temperature dependence of stationary gas mixture temperature catalyst

$$T_{g,\infty} = T - \frac{T_Q Y_{a,\infty}}{\left(\frac{1+Se}{Se} - \left(2-n\right)\frac{T_Q Y_{a,\infty}}{T} Le^m\right)}, \tag{6}$$

Maximum on the dependence $T_g(T)$ responses to critical condition of catalytic self-ignition with combustible gas impurities on the catalyst wire (particle) (fig. 2) and the minimum - catalytic extinction condition [4, 5]. The curve that lies between the points **i** and **e**, determines the conditions of ignition catalytic reaction in the preliminary heating of the catalyst to temperature above the ignition.

In the diffusion area $k >> \beta$ ($Se >> 1$) of (5) or (6) we have the equation for the wire temperature in flameless burning mode

$$T_{bur} = T_{g,\infty} + \frac{Q_a Y_{a,\infty} Le^{1-m}}{c_{pg}\left(1 - A_T Y_{a,\infty}\right)}, \tag{7}$$

Consideration of thermal diffusion (fig. 1b) is important in the analysis of the catalytic combustion of hydrogen on a platinum catalyst [6, 8]. So thermal

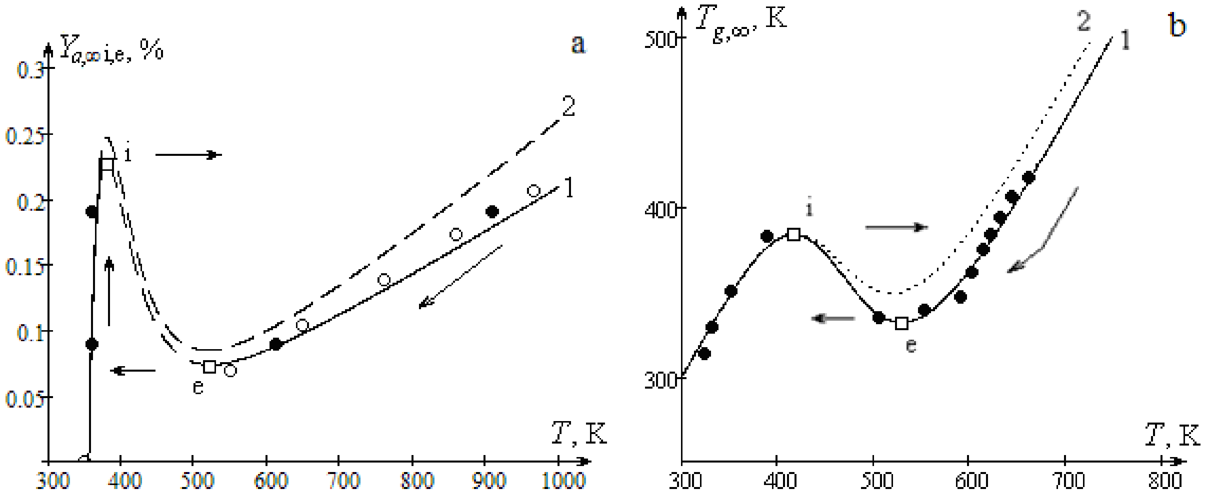

Fig. 1, a. Dependence of relative mass concentration of hydrogen in the air from stationary dimensionless temperature of platinum filament diameter 100 microns (Sh = 0.51). The temperature of the air-gas mixture is $T_{g,\infty}$ = 350 K. ●, ○ - experiment [8]. The calculation made by the equation (4).

Fig. 1, b. Temperature dependence of the air-gas mixture with hydrogen impurities from stationary temperature of platinum particles d = 100 mcm, $Y_{a,\infty}$, = 0.09%. The calculation made by the equation (6). Curve 1 – the impact of thermal diffusion; curve 2 – $\psi_T \neq 0$.

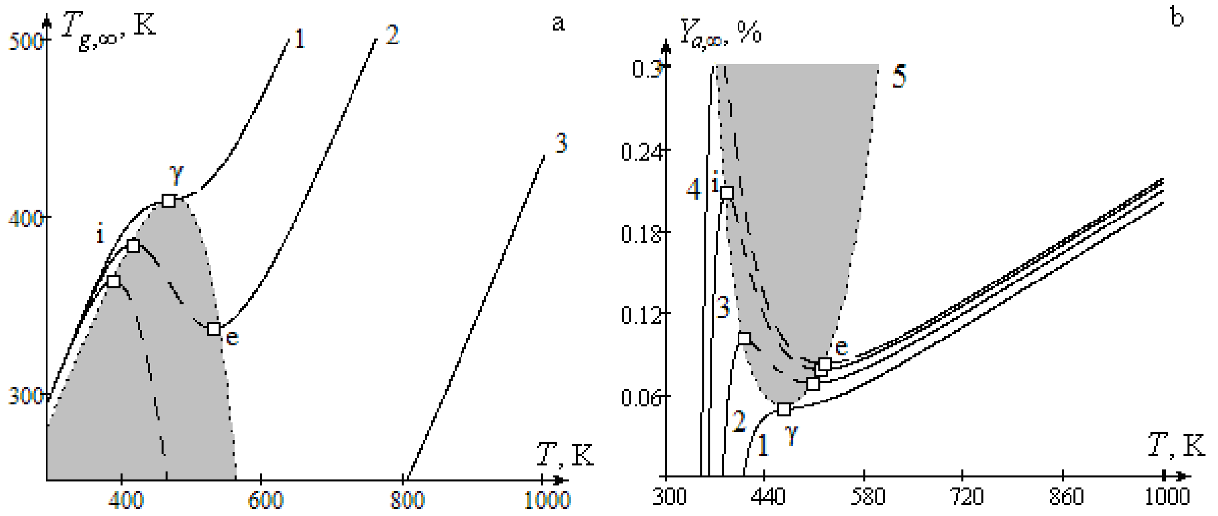

Fig. 2, a. Temperature dependence of the hydrogen-air mixture from a stationary temperature wire catalyst. Mass fraction of hydrogen in air $Y_{a,\infty}$: 1) 0.05% 2) 0.09% 3) 0.19%. Curve 4 calculated by dependence (10a).

Fig. 2, b. Dependence of hydrogen impurity concentration in the air from stationary temperature of wire catalyst. The temperature of the gas mixture $T_{g,\infty}$: 1) 410 K, 2) 380 K, 3) 360 K 4) 350 K. Curve 5 calculated by dependence (10, b)

diffusion hydrogen transfer increases the flameless hydrogen burning temperature (7), including the condition of extinction, and mostly have no effect to condition of catalytic self-ignition.

Using extremum condition in the dependences (4) and (6).

$$\partial Y_{a,\infty} \big/ \partial T \Big|_{i,e} = 0 \text{ або } \partial T_{g,\infty} \big/ \partial T \Big|_{i,e} = 0, \qquad (8)$$

let define equation for spinodal (fig. 2), which restricts area of the system parameters, which combines the catalytic ignition conditions (hysteresis area).

As a result of the use of the first condition (8) to (4) we obtain the following equality

$$\left(T - T_{g,\infty}\right)\frac{E}{RT^2} = \left(1 + \frac{k}{\beta}\frac{\rho_{gs}}{\rho_g}\right)\left(1 - \frac{\psi_T}{1+\psi_T}\frac{T_{g,\infty}}{T}\right), \qquad (9)$$

$$Se = \frac{k\rho_{gs}}{\beta\rho_g},\; B_T = \frac{\psi_T}{1+\psi_T}\frac{T_{g,\infty}}{T}.$$

Obtaining of this dependence we found that temperature dependence of the properties of flammable gas and gas mixture are considered as weak functions. Obtained equation is square equation relative to the temperature of the gas mixture, because thermal diffusion correction value for B_T depends on the temperature of the gas. However, taking to consideration that the characteristic values n = 1.75-1.82 and Lewis numbers Le = 3, the catalyst temperature T = 600 - 1000 K value B_T <0.1 and its weak dependence on the temperature of the gas mixture at T_g <450 K, it can be in first approximation calculated at a certain characteristic temperature of the gas mixture, as it was taken 410 K.

Thus, using (9) and (4), taking into account the mass transfer and thermal diffusion of combustible component we have system of two parametric equations (spinodal equations) describing critical conditions of catalytic self-ignition and extinction of hydrogen impurities on the catalyst particle:

$$\begin{cases} T_{g,\infty}\Big|_{i,e} = T - \dfrac{RT^2}{E}\left(1+Se\right)\left(1-B_T\right), & (10,a) \\ Y_{a,\infty}\Big|_{i,e} = \dfrac{c_{pg}RT^2}{Q_a Le^{1-m}E}\dfrac{\left(1+Se\right)^2}{Se}\dfrac{\left(1-B_T\right)}{\left(1+\psi_T\right)}. & (10,б) \end{cases}$$

Each of these relations $T_{g,\infty i,e}(T)$ and $Y_{a,\infty i,e}(T)$ determines the hysteresis area on appropriate stationary dependences $T_{g,\infty}(T)$ and $Y_{a,\infty}(T)$. To the left of the hysteresis area are low-temperature stationary states, right - high-temperature (catalytic combustion gases).

Analysis of (10a) and (10b) shows that the thermal diffusion of combustible gas reduces the critical temperature values of the gas mixture and fraction of combustible gas for its catalytic self-ignition and extinction on catalyst.

By increasing the temperature of the gas mixture and reducing the concentration of combustible gas occurs degeneration of hysteresis loop on temperature dependence of wire (particle) catalyst from concentration of combustible gas impurities (point γ). The temperature value of the gas mixture at the point of critical conditions degeneration and becomes a characteristic temperature for estimation the parameters of the gas mixture.

With the increase in the diameter of the catalyst wire (particle) (fig. 3) decreases degeneration temperature, and hence hysteresis heat transfer area of the catalyst. Critical value of degeneration concentration also reduced. Catalytic self-ignition takes place in the kinetic area (Se <1) and extinction in transition area (1 <Se <5). When there is a degeneration of critical conditions diffusion-kinetic ratio goes close to 1.

The analysis showed that at the point of critical conditions degeneration for thin catalyst wires coefficient

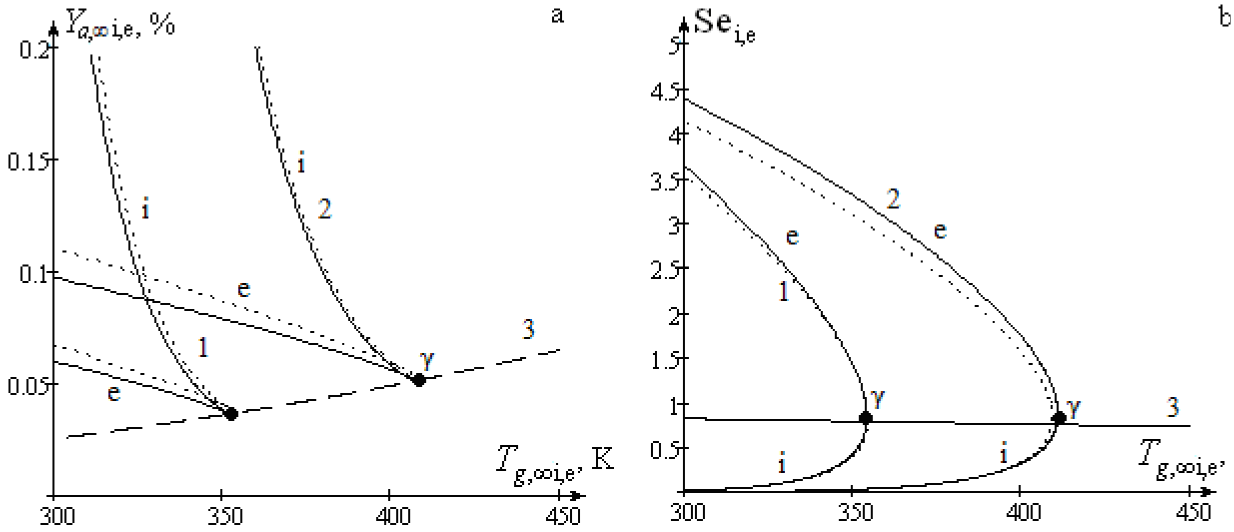

Fig. 3. Dependence of critical: a) the concentration of hydrogen b) diffusion-kinetic relation from temperature of the hydrogen-air mixture for catalyst filament diameter 1) 1000 and 2) 100 mcm. The solid curve is the impact of thermal diffusion; dotted line – $\psi_T \neq 0$. Curve 3 is the curve degeneration of equations (11).

B_T is small. In this case, the parameters degeneracy point (point γ), possible to obtain, using additional condition $\partial Y_{a,\infty i,e}/\partial T\big|_{\gamma} = 0$ or $\partial T_{g,i,e}/\partial T\big|_{\gamma} = 0$:

$$T_{g,\infty}\Big|_{\gamma} = T\cdot\left(1-\frac{2T/T_E}{1+2T/T_E}\right),\quad Y_{a,\infty}\Big|_{\gamma} = \frac{T^2}{T_E T_Q}\cdot\frac{4}{1-\left(2T/T_E\right)^2}, \tag{11, a}$$

$$d_{\gamma}\Big| = \frac{D_a Sh}{k}\cdot\frac{1-2T/T_E}{1+2T/T_E},\quad Se_{\gamma}\Big| = \frac{1-2T/T_E}{1+2T/T_E},\quad T_E = \frac{E}{R}, \tag{11, б}$$

The dependences represent the parameters connection of critical conditions degeneration in parametric form (parameter - temperature catalyst). For example, for platinum wire diameter 100 mcm corresponds concentrations of hydrogen in air, conforms to degeneration, is about 0.052 % by weight (0.75% by volume).

On the other side when increasing the concentration of flammable gas may make catalytic ignition of it, burning will keep by itself even at normal temperature conditions. With the mass fraction of hydrogen in mixture of more than 1% catalyst extinction temperature is T_e < 293 K.

Thus, we formulated areas of conditions, in which there is hysteresis heat and mass exchange and linear temperature dependence of wire (particle) catalyst from concentration of combustible gas impurities and temperature of the air-gas mixture in the one-sided and parallel formation of similar to gas products in the diffusion flameless combustion mode and where possible neglect radiation heat loss.

Conclusions

A study of the peculiarities of diffusion-kinetic ratio, Lewis criterion, thermal diffusion and reaction scheme on characteristics of heat and mass exchange hysteresis and flameless combustion of air-gas mixture with impurities of combustible gases (hydrogen) on platinum particles and wires lead to the following conclusions:

Found that thermal diffusion hydrogen transfer increases the temperature catalytic combustion of air-gas mixture with hydrogen impurities, significantly reduces the temperature of the gas mixture of hydrogen and a share in it to spontaneous extinction and has almost no effect on the critical condition of the catalytic self-ignition air-gas mixtures with hydrogen impurities. Increasing of temperature in air-gas mixture leads to heat emission decrease and therefore reduces the concentration of ignition and extinction. The concentration of ignition is reduced greater, due to the occurrence of process in the kinetic area. Found and analyzed areas of critical conditions for ignition and extinction in air-gas mixtures with impurities of combustible gas (hydrogen), which are setting the heat and mass exchange hysteresis on dependences like: particle temperature from the air-gas mixture temperature, impurity concentration from combustible gas and particle diameter (wire) catalyst.

It is shown diffusion-kinetic ratio increases in the catalytic hydrogen ignition to increase in gas mixture temperature, and reduced in the catalytic extinction, and its importance approaches unity in the degeneration of

the hysteresis loop.

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Вплив термодифузії на границі гістерезису каталітичного горіння домішок водню на платиновому дротику

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В роботі представлені результати комплексних досліджень механізмів гістерезису тепломасообміну та каталітичного безполум'яного стаціонарного стійкого горіння газоповітряних сумішей з домішками водню на платинових дротиках і частинках. З врахуванням термодифузії побудовано аналітичні моделі гістерезису тепломасообміну і кінетики горіння домішок горючих газів на металевій частинки (дротику) каталізатора при наявності тільки однієї односторонньої реакції в залежності від концентрації домішки горючого газу та температури газоповітряної суміші. Термодифузійний перенос водню збільшує температуру каталітичного горіння газоповітряних сумішей з домішками водню і практично не впливає на критичні умови каталітичного займання суміші, на відміну від умов каталітичного погасання. Запропоновано метод аналітичного отримання гістерезисних областей тепломасообміну ниток (частинок) каталізатора, всередині яких спостерігається каталітичне запалювання, а ззовні – стаціонарні стани окислення та каталітичного горіння малих домішок горючого газу в повітрі.

Ключові слова: металеві каталізатори окислення, нитка, водень, гістерезис тепломасообміну, самозаймання, погасання, поверхневе (безполум'яне) горіння.