

V.V. Kalinchak¹, A.S. Chernenko¹, A.F. Fedorenko¹, A.N. Sofronkov², V.V. Kramarenko¹

Catalyst Particle Porosity Effect upon Flameless Combustion Characteristics

¹I.I. Mechnikov Odessa National University, Odessa, Ukraine, chernalex@ukr.net

²Odessa State Ecological University, Odessa, Ukraine, teplophys@onu.edu.ua

The problem of heat and mass transfer of a porous catalyst particle is considered. On the her surface, including the inner surface of the pores, an irreversibly heterogeneous first-order reaction proceeds. It has been analytically shown that in a heated gas mixture, the catalyst's porosity reduces the minimum impurity's concentration of catalytic spontaneous combustion in the mixture and increases the catalyst particle's corresponding diameter. This concentration corresponds to the external kinetic and internal diffusion reaction's modes.

Keywords: metal oxidation catalysts, porosity, ignition, surface (flame-free) combustion.

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Introduction

Multiple heterogenous chemical oxidation reactions and flameless combustion of combustible gases admixtures occur on porous catalyst particles staying within gas/air mixture flow. Critical conditions of flameless combustion depend on size of the particle specific surface area and on combustible gases concentration. Platinum-group metals and metallic oxides of variable valence act as catalysts. Platinum-group metals are applied either in the form of threads, or are speckled into carrier's particles. The majority of active areas are located inside pores in oxidation catalyst [1]. Catalytic reaction occurs after the reagent molecules penetrate through the boundary level surrounding catalyst's particles (external diffusion) and afterwards through the particle's pores (internal diffusion). The resulting interaction between thermal conductivity, reagents diffusion, reaction products and chemical reaction plays an important part in catalyst's efficiency. Ingredients transfer inside the catalyst should be taken into account if the pores' diameter exceeds 50 nm. Such solid catalyst particles with large pores are applied, for instance, in oxidation reactions, membrane reactors and in certain biological applications.

Porosity and nanostructure are the most universal

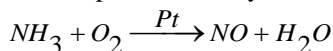
peculiarities of heterogenous solid catalysts capable to determine accessibility of particular active areas, reaction mechanism and selectivity of desirable products [2]. However, thermal radiation losses should be taken into account for large catalyst packs, even with comparatively low radiation factor typical for metallic oxidation catalysts ($\epsilon = 0.1 - 0.2$).

Problem of diffusion inside porous catalyst particles is dealt with for a rather long time [3-5]. Mostly, attention is focused on simultaneous review of convection processes, diffusion processes and reaction flow inside porous catalyst. However, critical conditions of catalytic reaction's steady running and porosity effect upon reaction characteristics are generally neglected.

This work is aimed to establish the catalyst porosity effect (mean specific surface of pores) upon crucial characteristics of high-temperature heat and mass exchange and kinetic parameters of heterogenous catalytic combustion for minor combustion gases' quantities in heated air. Here the attention is also paid to combustible gases external and internal mass transfer to the particle surface and into the depth of chemical reaction penetration into the particle.

Research objective

The review is carried on referring to ammonia oxidation reaction on platinum catalyst:



with parameters, as follows $Q_a = 13.3$ MJ/kg NH_3 , $E = 139$ kJ/mole, $k_0 = 13 \cdot 10^{13}$ m/sec.

According to contact principle, suppose that active combustible component molecules of gaseous environment collide with oxygen molecules absorbed by the catalyst surface generating reaction products of heterogenous catalytic reaction. Rate of heterogenous catalytic reaction on the catalyst particle surface and on the surface with combustible component available in gaseous environment is directly related with relative mass concentration of such a combustible component close to catalyst's surface Y_{as} :

$$W_a = W_{as} + W_{av} = k_{\Sigma} \rho_{gs} Y_{as} = (k + k_v) \rho_{gs} Y_{as}, \quad (1)$$

$$\rho_{gs} = \rho_{g0} \left(\frac{T_0}{T} \right) \cdot \left(\frac{P}{P_0} \right)$$

with W_a , W_{as} , W_{av} – total rate of catalytic reaction for combustible substance of the outside surface and at the pores' surface, respectively, kg/(m²sec); k_{Σ} , k , k_v – internal reaction of combustible with oxygen total, actual and efficient constant values, respectively, m/sec; T – catalyst's temperature, K; ρ_{gs} – gaseous mixture density near the particle's surface kg/m³; P – pressure, Pa.

Heterogenous catalytic reaction speed constant in this case is represented by a sum of reaction constants on the external surface and inside pores.

Actual catalytic reaction speed constant on the external surface and on pores surface of catalyst's particle increases as the temperature grows subject to Arrhenius equation:

$$k = k_0 \exp\left(-\frac{E}{RT}\right), \quad (2)$$

with k_0 – pre-exponential multiplier, m/sec; E – activation energy, J/mole, R – universal gas constant, J/(mole K).

Heat conductivity equation for internal reactions and reaction running on the surface of a porous catalyst particle may be represented, as below:

$$c_c \rho_c \frac{\partial T}{\partial t} = \frac{1}{r^s} \frac{\partial}{\partial r^2} \left(r^s \lambda_c \frac{\partial T}{\partial r^2} \right) + q_{ch,p},$$

$$T(t=0) = T_b, \quad (3)$$

$$q_{ch,p} = Q_f \frac{\sum N_i S_i}{V_c} k \rho_{gs} Y_a = Q_f F_v k \rho_{gs} Y_a,$$

with s – particle shape factor (0 – plate, 1 – cylinder, 2 – sphere), F_v – specific pores' area (total pores' surface area value divided by particle's volume), m⁻¹; Q_f – reaction's thermal effect per 1 kg of combustible gas,

J/kg; N_i – number of pores with S_i surface area; V_c – catalyst's volume, $q_{ch,p}$ – heat generation power on pores' surface per particle's volumetric unit, W/m³.

General heat flow in the particle's center takes a zero

$$\text{value: } -r^s \lambda_c \left. \frac{\partial T}{\partial r} \right|_{r=0} = 0.$$

Boundary condition on catalyst surface may be represented, as below, taking into account reaction running on its surface:

$$-\lambda_c \left. \frac{\partial T}{\partial r} \right|_{r=d/2} + q_{ch,s} = q_g + q_w,$$

$$q_w = \varepsilon \sigma (T^4 - T_w^4), \quad q_{ch,s} = Q_f k \rho_{gs} Y_{as},$$

$$q_g = \beta c_g \rho_g L e^{1-m} (T - T_g).$$

The problem may be simplified by means of taking into account correlation between heat conductivity factors for gaseous mixture and solid catalyst and between thermal conductivity factors. In case when the catalyst heat conductivity factor exceeds substantially the respective heat conductivity of gaseous mixture the temperature distribution inside the catalyst may be ignored. Thus dependence of temperature on coordinate may be ignored. It enables to average temperature throughout the entire catalyst volume. Thus, non-steady state heat balance equation for porous catalyst may be written in the format, as follows:

$$\frac{d}{6} c_c \rho_c \frac{dT}{dt} = q_{eff}, \quad T(t=0) = T_b. \quad (4)$$

$$q_{eff} = q_{ch} - q_h, \quad q_{ch} = q_{ch,s} + q_{ch,v}, \quad q_h = q_g + q_w,$$

$$q_{ch,v} = Q_a W_{av}, \quad W_{av} = k \rho_{gs} \frac{F_v d}{6} \langle Y_a \rangle_v = k_v \rho_{gs} Y_{as},$$

with q_{eff} – efficient volumetric heat release rate, W/m².

Internal diffusion problem should be solved to calculate internal reaction rate and combustible substance concentration profile inside the particle:

$$\rho_c \frac{\partial Y_a}{\partial t} = \frac{1}{r^s} \frac{\partial}{\partial r^2} \left(r^s D_a \frac{\partial Y_a}{\partial r^2} \right) - W_a, \quad (5)$$

$$W_a = \frac{\sum N_i S_i}{V_c} k \rho_{gs} Y_a = F_v k \rho_{gs} Y_a,$$

with existing boundary conditions inside the particle

$$r^s D_v \rho_{gs} \left. \frac{\partial Y_a}{\partial r} \right|_{r=0} = 0.$$

And on the particle's surface

$$W_{av} = D_v \rho_{gs} \left. \frac{\partial Y_a}{\partial r} \right|_{r=d/2}, \quad W_{as} + W_{av} = j_a,$$

$$W_{as} = k \rho_{gs} Y_{as}.$$

Referring to outlined film model, combustible component mass flow density j_a on the catalyst surface (mass transferred per time unit to the catalyst's surface

unit) taking into account mass transfer due to thermal diffusion effect [6] may be identified, as follows:

$$j_a = \beta \rho_g \left((Y_a - Y_{as}) + \frac{k_T}{T} (T - T_g) \cdot Le^m \right), \quad (6)$$

$$\beta = \frac{D_a Sh}{d}, \quad Sh = Nu_D, \quad D_a = D_0 \left(\frac{T_{g^*}}{T_0} \right)^n \cdot \frac{P_0}{P},$$

$$\rho_g = \rho_{g0} \left(\frac{T_0}{T_{g^*}} \right) \cdot \left(\frac{P}{P_0} \right), \quad T_{g^*} = \frac{T + T_g}{2}.$$

Evaluation of the Bio's diffusion number

$$Bi_D = \frac{\beta r_s}{D_v} = \frac{D_a Sh}{D_v \cdot 2}$$

shows, that it exceeds 1. It means that combustible substance distribution inside the catalyst's particle may not be ignored. On the other side, correlation between combustible's internal diffusion factor to the catalyst's thermal conductivity factor exceeds 1. It enables us to review the internal diffusion problem as a quasi-neutral.

Combustible gas surface relative mass concentration may be calculated subject to steady rate of chemical reaction and mass transfer rate to the particle's surface:

$$k_{\Sigma} \rho_{gs} Y_{as} = \beta \rho_g \left((Y_a - Y_{as}) + \frac{k_T}{T} (T - T_g) \cdot \left(\frac{D_a}{a_g} \right)^b \right),$$

Solution of the above equation may be represented, as follows:

$$Y_{as} = Y_a (1 + \Psi_T) \left(1 + \frac{k_{\Sigma} \cdot \rho_{gs}}{\beta \cdot \rho_g} \right)^{-1} = Y_a \frac{1 + \Psi_T}{1 + Se}, \quad (7)$$

$$Se = \frac{k_{\Sigma} \cdot \rho_{gs}}{\beta \cdot \rho_g}, \quad \Psi_T = \frac{(T - T_g)}{T} Le^m (2 - n),$$

with Se – Semyonov kinetic number, $Le = D_a/a_g$ – Lewis' criterion, Ψ_T – thermal diffusion correction value (concentration increase due to temperatures'

difference).

Thus, the more is Lewis' criterion, as is indicated in formula (6), the higher is the thermal diffusion contribution into combustible component general mass transfer process, which is the most substantial in catalytic oxidation of hydrogen.

Internal reaction area

Having solved the quasi-stationary problem for internal reaction efficient constant (5) k_v the following formulae may be obtained:

$$k_v = \frac{D_v}{r_s} (Se_v cth Se_v - 1), \quad (8)$$

$$Se_v = \sqrt{\frac{kr_s^2 F_v}{D_v}} = \frac{r_s}{h}, \quad h = \sqrt{\frac{D_v}{kF_v}}, \quad (9)$$

with r_s – particle's external surface radius, m; D_v – combustible gas internal diffusion factor inside the pores, m²/sec, Se_v – Semyonov value number, indentifying relation between chemical reaction running on the pores' surface to combustible substance mass transfer into the particle's pores; h – chemical reaction penetration depth into the particle.

Combustible substance internal diffusion factor may be determined by the particle's porosity and combustible substance diffusion factor for gaseous phase [7]:

$$D_v = \chi^2 \cdot D_a, \quad \chi = 1 - \frac{\rho}{\rho_{tr}}$$

with χ – particle's porosity (volume of pores ratio to entire particle's volume); ρ_{tr} – true density of the particle substance.

Now let us review two areas where chemical reaction runs. They are internal kinetic and diffusive.

The *internal kinetic zone* is observed with comparative low temperatures and minor particle diameters, for which $Se_v < 0.55$. In this case:

$$Se_v cth Se_v - 1 = Se_v \frac{\exp Se_v + \exp(-Se_v)}{\exp Se_v - \exp(-Se_v)} - 1 \approx \frac{1 + \frac{Se_v^2}{2}}{1 + \frac{Se_v^2}{6}} - 1 \approx \frac{Se_v^2}{3} \left(1 + \frac{Se_v^2}{6} \right)^{-1}$$

The second expression taken in brackets may be ignored in comparison with 1. The resulting internal reactive constant increases in linear fashion as the particle diameter increases:

$$k_v = \frac{2D_v}{d} \frac{Se_v^2}{3} = k \frac{F_v d}{6}. \quad (10)$$

With $Se_v = 1$ fault of formula (10) amounts to 6 %, and it may be applied for $Se_v < 1.5$. within up to 15 % accuracy.

Further increase in temperature and particle diameter

may lead to chemical reaction kinetics shifting to the *internal diffusion zone*, where $Se_v \gg 1$. For $Se_v > 5$ we have $cth Se_v \gg 1$. Thus internal reactive constant in this case does not depend on the particle's diameter:

$$k_v = \frac{2D_v}{d} Se_v = \frac{2D_v}{d} \sqrt{\frac{kF_v d^2}{4D_v}} = \sqrt{kD_v F_v}. \quad (11)$$

For $Se_v > 2$ and $Se_v < 5$ internal reactive constant may be described approximately with relation showing proportional relationship with the particle's diameter:

$$k_v = \frac{2D_v}{d}(Se_v - 1) = \frac{2D_v}{d} \left(\sqrt{\frac{kF_v d^2}{4D_v}} - 1 \right) = \sqrt{kD_v F_v} - \frac{2D_v}{d} \quad (12)$$

Thus, approximated internal reactive constant value may be applied in analytical calculations depending on Se_v , criterion value.

Stationery stable and critical states

Here all the stationery states (both stable and critical) are reviewed referring to the catalyst temperature. They are determined by combustible component concentration. In this view, relation is subject to review between combustible substance concentration and catalyst temperature obtained from stationary condition (4):

$$Y_a = \left(\frac{\beta}{k + k_v} + 1 \right) \left(\frac{c_g (T - T_g)}{Q_a L e^{1-m}} + \frac{\varepsilon \sigma (T^4 - T_w^4)}{\beta Q_a \rho_g} \right) \quad (13)$$

Catalytic combustion temperature and low-temperature oxidation increase as the oxidant concentration grows Fig. 1). The time-independent relation $Y_a(T)$, indicates, that maximum point corresponds to critical condition of gases self-ignition (point i), and minimum point corresponds to critical condition of self-fading (point e).

Abnormal drop in catalyst stationery temperature with increasing ammonium concentration Y_a is observable within $Y_{ai} < Y_a < Y_{ae}$ interval (unstable critical states corresponding to critical initial catalyst temperature T_{bi}). With catalyst initial temperature exceeding the value corresponding to stationery line $Y_a(T_{bi})$, the catalyst temperature grows until it achieves stable catalytic combustion temperature. If initial temperature $T_b < T_{bi}$, the catalyst temperature will decrease close to low-temperature oxidation value.

Catalyst porosity reduces critical concentration value

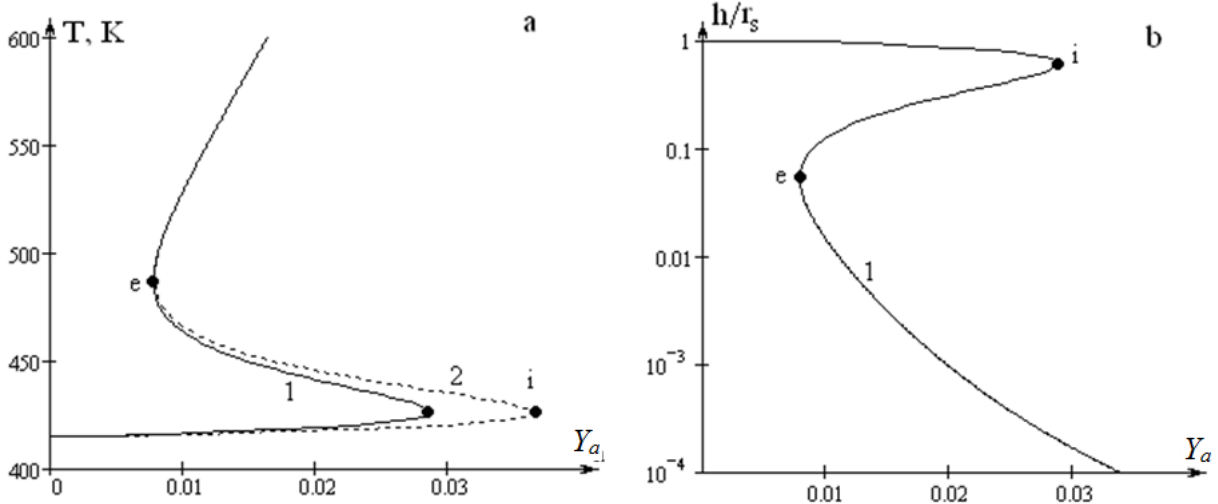


Fig. 1. Relations between a) stationery temperature and b) reaction penetration depth into pores and combustible substance concentration (line 1) and ignoring the porosity (line 2): particle diameter $d_* = 1000 \mu\text{m}$ at $T_g = 420 \text{ K}$, $T_w = 293 \text{ K}$, $F_v = 10^3 \text{ m}^{-1}$, $\chi = 0.1$.

Table 1

Catalyst particle porosity effect on critical ammonium concentration (%) in air for particle $d_* = 1000 \mu\text{m}$

| Porosity | Formula applicable for k_v calculation | $T_g = 420 \text{ K}$, $T_w = 293 \text{ K}$ ($T_i = 426 \text{ K}$) | | $T_g = 400 \text{ K}$, $T_w = 293 \text{ K}$ ($T_i = 406 \text{ K}$) | |
|---|--|--|---------------------|--|---------------------|
| | | Solid particle ($F_v = 0$) | – | 3.65 | – |
| Porous particle ($F_v = 10^3 \text{ m}^{-1}$) | (8) | 2.86 | $Se_v = 1.7$ by (9) | 16.5 | $Se_v = 0.6$ by (9) |
| | (10) | 2.76 | | 16.4 | |
| | (11) | 2.34 | | 8.87 | |
| | (12) | 2.98 | | – | |
| Porous particle ($F_v = 10^4 \text{ m}^{-1}$) | (8) | 1.55 | $Se_v = 6.2$ by (9) | 6.00 | $Se_v = 2.2$ by (9) |
| | (10) | 0.92 | | 5.11 | |
| | (11) | 1.42 | | 4.12 | |
| | (12) | 1.55 | | 6.31 | |

required for ammonium ignition in air on the catalyst particle. In this case chemical reaction in low-temperature zone runs practically within entire catalyst volume up to the self-ignition point. It is illustrated by Se proximity to 1 (Table 1, Fig. 1b). Fading concentration critical value does not practically depend on the catalyst porosity.

It is rather difficult to apply formula (8) to analytical search for critical states. Referring to Table 1 approximated relations (10), (11) and (12) may be applied to identify critical states depending on particle specific porosity surface area and surrounding gaseous mixture temperatures. Formula (10) with $Se_{vi} < 2$ may be reasonably applied to calculate internal reactive constant. Formula (11) is applicable for $Se_{vi} > 2$. As the gaseous mixture temperature decreases, even by 20 K only, the internal Semyonov value number for critical point decreases triple.

Fig. 2 represents critical states for ammonium ignition in air on catalyst particle depending on the

particle dimensions with various porosity, as a plurality of points being extremum of function (13).

Taking into note thermal losses for radiation leads to formation of diameter limiting value for gases self-ignition zone on catalyst particles surface. Applying porous catalyst, even with small specific pores surface area (e.g., 10^3 m^{-3}) leads to substantial decrease of minimum critical value of combustible component concentration, which, being exceeded, provokes catalytic ignition on the catalyst surface. Particle diameter increases with porosity increase.

It should be noted, that critical states for self-ignition correspond to external kinetic area where the chemical reaction runs and to internal diffusion area (for $d_* > 300 \text{ }\mu\text{m}$, $Se_v > 2$). It enables to apply formula (11) to identify location of minimum point to calculate internal reactive constant.

Stationary condition taking into account porosity looks, as below:

$$Q_a Y_a \rho_g \left(k + \sqrt{k D_v F_v} - \frac{2 D_v}{d} \right) = \alpha (T - T_g) - \varepsilon \sigma (T^4 - T_w^4). \quad (14)$$

Alteration made in a formula part indicating porosity of an item:

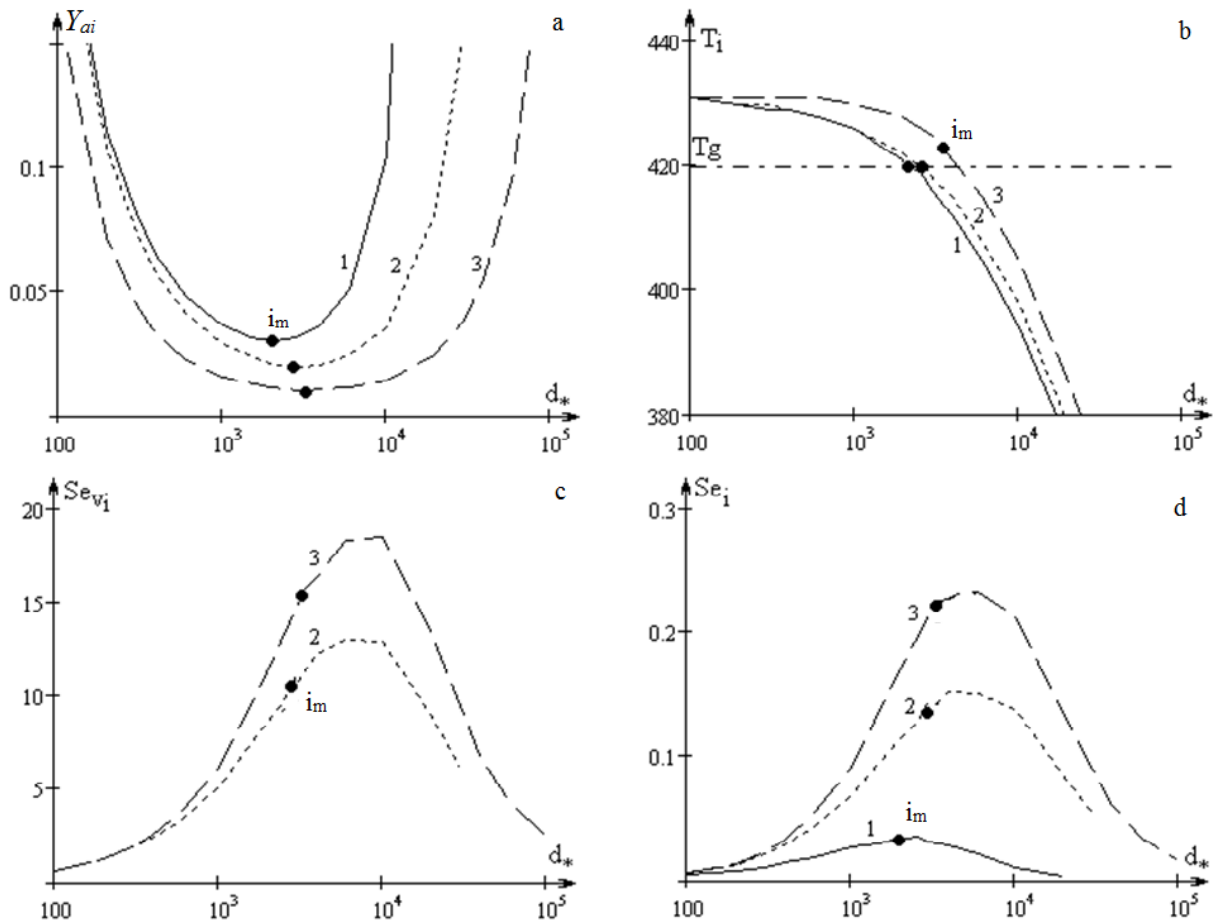


Fig. 2. Relations between a) combustible substance critical concentration and b) catalyst critical temperature, c) internal Semyonov value number and d) Semyonov value number and diameter at $T_g = 420 \text{ K}$, $T_w = 293 \text{ K}$. Curves: 1 – solid particle; 2 – porous particles, $F_v = 10^3 \text{ M}^{-1}$, $\chi = 0.1$; and 3 – $F_v = 10^4 \text{ M}^{-1}$, $\chi = 0.1$.

$$\frac{2D_v}{d} = b\alpha, \text{ where } b = \frac{D_v}{3\lambda_g Nu}, \quad \alpha = \beta c_g \rho_g Le^{1-m}.$$

Thus stationary condition may be described, as follows:

$$Q_a Y_a \rho_g \left(k + \sqrt{k D_v F_v} - b\alpha \right) = \alpha (T - T_g) + \varepsilon \sigma (T^4 - T_w^4).$$

The equation $\frac{\partial q_{ch}}{\partial \alpha} = \frac{\partial q_h}{\partial \alpha}$ may be applied to identify

minimum critical state point, with q_{ch} i q_h – left and right parts of the equation (14). Thus,

$$-Q_a Y_a \rho_g b = (T - T_g).$$

Temperature corresponding to minimum point

(minimum ignition point i_m): $T_{i_m} = T_g - \frac{Q_a Y_a \rho_g D_v}{3\lambda_g Nu}$.

Normally, the subtrahend value is rather small which leads to difference between T_{i_m} from gaseous mixture temperature T_g in 1 K. It enables to take $T_{i_m} \approx T_g$. Substitution of this allowance into (13) enables to obtain combustible gas concentration value corresponding to minimum point (pt. i_m):

$$Y_{a_{i_m}} = \frac{\varepsilon \sigma (T_g^4 - T_w^4)}{Q_a \rho_g k_0} \left(1 + \sqrt{\frac{D_v F_v}{k(T_g)}} - \frac{2D_v}{d \cdot k(T_g)} \right)^{-1} \exp\left(\frac{E}{RT_g}\right). \quad (15)$$

$\frac{\partial q_{ch}}{\partial T} = \frac{\partial q_h}{\partial T}$ may be applied to calculate critical diameter in the minimum point.

$$Q_a Y_a \rho_g \left(k + \frac{1}{2} \sqrt{k D_v F_v} \right) \cdot \frac{E}{RT^2} = \alpha + 4\varepsilon \sigma T^3.$$

Applying $T_{i_m} \approx T_g$ and (13), diameter may be calculated, as follows:

$$\varepsilon \sigma (T_g^4 - T_w^4) \left(\frac{k + \frac{1}{2} \sqrt{k D_v F_v}}{k + \sqrt{k D_v F_v} - b\alpha} \right) = \frac{\alpha RT_g^2}{E} + 4\varepsilon \sigma T_g^3 \frac{RT_g^2}{E}.$$

$$i \quad \frac{1}{d} \cdot \frac{\lambda_g Nu RT_g^2 / E}{\varepsilon \sigma T_g^4} \Big|_{i_m} = \left(1 - \frac{T_w^4}{T_g^4} \right) \left(\frac{k(T_g) + \frac{1}{2} \sqrt{k(T_g) D_v F_v}}{k(T_g) + \sqrt{k(T_g) D_v F_v} - \frac{2D_v}{d}} \right) - \frac{4RT_g}{E}. \quad (16)$$

Table 2 contains comparative combustible concentration values and catalyst particle diameter describing border conditions of ignition calculated sing formulae (15) and (16).

Comparing the obtained formulae with similar in which reaction in pores was not taken into account [8], enables to identify a multiplier defining porosity effect on mixture concentration limit value and catalyst particle diameter:

$$Y_{a_{i_m}} \sim \left(1 + \sqrt{\frac{D_v F_v}{k(T_g)}} - \frac{2D_v}{d \cdot k(T_g)} \right)^{-1} \quad \text{and}$$

$$\frac{1}{d_{i_m}} \sim \left(\frac{k(T_g) + \frac{1}{2} \sqrt{k(T_g) D_v F_v}}{k(T_g) + \sqrt{k(T_g) D_v F_v} - \frac{2D_v}{d}} \right). \quad (17)$$

So, as the pores specific surface area increases value

$Y_{a_{i_m}}$ decreases. Catalyst material porosity effect χ according to (17) is more complicated.

Catalyst porosity effect upon induction period

Fig. 3 illustrates time relation of catalyst temperature T and Semyonov value Se during ammonium catalytic oxidation both taking into account and ignoring particles porosity for catalytic ignition case. Apparently, porous particle naturally reduces time of high-temperature oxidation mode gaining (induction period).

Total time period may be split into three stages. The first represents inert preheating. Semyonov value is extremely small indicating minor chemical heat emission ratio. The second stage represents particle's chemical heating due to chemical heat emission as chemical

Table 2

Catalyst particle porosity effect on limiting critical conditions of ammonia ignition in air ($T_g = 420$ K)

| | $F_v = 10^3 \text{ m}^{-1}$ | | $F_v = 10^4 \text{ m}^{-1}$ | |
|----------------------------|---|---------------------|---|---------------------|
| | $Se_{v_{i_m}} = 10.9, \text{ з Fig. 2}$ | | $Se_{v_{i_m}} = 15.1, \text{ з Fig. 2}$ | |
| | Value ref. Fig. 2 | solution (15), (16) | Value ref. Fig. 2 | solution (15), (16) |
| $Y_{a_{i_m}}$ | 0.0199 | 0.0243 | 0.0104 | 0.0114 |
| $d_{*_{i_m}}, \mu\text{m}$ | 2950 | 2320 | 3350 | 3350 |

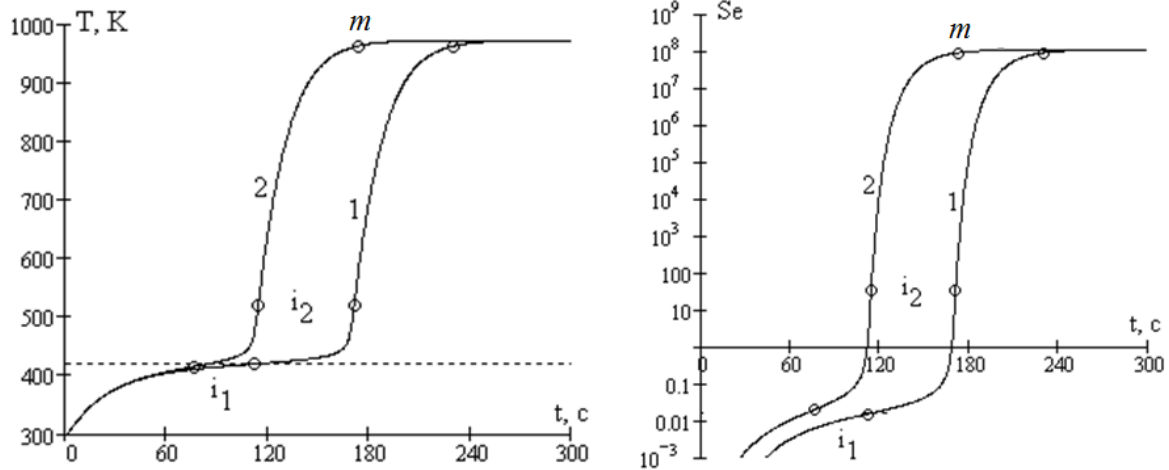


Fig. 3. Time relations a) platinum particle temperature and b) Semyonov value with ammonium concentration $Y_a = 6.0\%$ for $T_g = 420$ K, $T_w = 293$ K, $T_b = 293$ K, $d/Nu = 1000 \mu\text{m}$. 1 – solid particle, 2 – porous particle $F_v = 10^3 \text{ m}^{-1}$, $\chi = 0.1$.

Table 3

Porosity effect upon induction period stages duration $Y_a = 6.0 \%$, $T_g = 420$ K, $T_w = 293$ K, $T_b = 293$ K, $d^* = 1000 \mu\text{m}$, $\chi = 0.1$

| $F_v, \text{ m}^{-1}$ | $t_1, \text{ sec}$ | $t_2, \text{ sec}$ | $t_3, \text{ sec}$ | $t_{ind}, \text{ sec}$ | $T_1, \text{ K}$ | $T_3, \text{ K}$ |
|-----------------------|--------------------|--------------------|--------------------|------------------------|------------------|------------------|
| 0 | 111.6 | 59.1 | 58.8 | 229.5 | 420 | 965 |
| 10^3 | 75.9 | 38.1 | 58.8 | 172.8 | 415 | 965 |
| 10^4 | 53.7 | 29.1 | 58.8 | 141.6 | 407 | 965 |
| 10^5 | 34.8 | 24.0 | 58.8 | 117.6 | 388 | 965 |
| 10^6 | 22.50 | 19.8 | 59.1 | 101.4 | 367 | 965 |

reaction runs in kinetic zone. The third stage represents particle heating due to chemical heat emission as the chemical reaction runs in diffusion zone.

Porosity effect is shown in Table 3. Decrease of the first stage with increasing porosity is caused by decrease of the upper limit of this stage. Chemical reaction commences earlier due to porosity than with solid particles.

Decrease of the second stage is caused by substantial role played by internal reaction running in kinetic zone. Duration of the third stage does not depend on the particle's porosity. Combustible component does not reach full depth of a particle with chemical reaction running in external diffusion zone.

Conclusions

Combustible gas oxidation reaction inside porous particle of catalyst leads to decrease in combustible gas minimum concentration, which, once exceeded provokes

catalytic ignition on catalyst particle surface. The obtained formula enables to analyze porosity effect on critical value and corresponding particle diameter. Increase in catalyst porosity leads to drop of induction period due to reduction in preheating time and chemical heating time with the reaction running in kinetic zone.

Kalinchak V.V. - Doctor of Science (Physics), Professor, Department of General Physics and Physics of Thermal Energy and Chemical Processes;

Chernenko A.S. - Ph.D., Associate Professor, Department of General Physics and Physics of Thermal Power and Chemical Processes;

Fedorenko A.V. - postgraduate student of the Department of General Physics and Physics of Thermal Power and Chemical Processes;

Sofronkov A.N. - Doctor of Technical Sciences, Professor of the Department of Environmental Chemistry;

Kramarenko V.V. - PhD student.

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В.В. Калінчак¹, О.С. Черненко¹, А.В. Федоренко¹,
О.Н. Софронков², В.В. Крамаренко¹

Вплив поруватості частинки каталізатора на характеристики безполуменового горіння

¹Одеський національний університет імені І.І. Мечникова, Одеса, Україна, chemalex@ukr.net

²Одеський державний екологічний університет, Одеса, Україна, teplophys@onu.edu.ua

Розглядається задача тепломасообміну поруватої частинки каталізатора, на поверхні якої, включаючи внутрішню поверхню пор, протікає необернена гетерогенна реакція першого порядку. Аналітично показано, що в нагрітій газовій суміші поруватість каталізатора сприяє зменшенню мінімальної концентрації каталітичного самозаймання домішки в суміші та збільшенню відповідного діаметру частинки каталізатора. Цій концентрації відповідає зовнішній кінетичний та внутрішній дифузійний режими протікання реакції.

Ключові слова: металеві каталізатори окислення, поруватість, займання, поверхнєве (безполум'яне) горіння.