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Improvement of the catalytic monoliths efficiency for CO oxidation using non-uniform active component distribution along the monolith length

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Abstract

It is shown that the efficiency of catalytic packages can be improved using two approaches. The monotone increase of the active component concentration towards the monolith outlet is shown optimal for minimization of the total active component loading at the preserved purification degree. To resolve the problem of achieving the maximal purification degree at a fixed quantity of the active component, it is preferable to concentrate the active component near the duct entrance.

Keywords: Distribution; CO oxidation; Monolith; Catalyst; Simulation

1. Introduction

The now challenging problem of exhaust gases neutralization of diesel internal combustion engines is one of cleaning from toxic impurities at relatively low gas temperature at the starting engine operation. The problem is resolved by application of catalysts for reliable low-temperature oxidation of CO [1,2].

It is common knowledge that the supported platinum-containing catalysts are the most effective to CO oxidation [1,3]. The usual platinum concentration in the CO oxidation catalysts equals 0.02–0.2 wt.% [1]. Taking into account that the cordierite support is predominant in the total weight of the monolith, the platinum concentration in the proper catalytically active layer is higher by an order of magnitude to reach several percent. With regard to the high cost of platinum, the problem of diminishing the platinum loading in the catalysts for CO oxidation at the same level of gas cleaning is of vital importance.

Along with development of new types of low-platinum catalysts for CO oxidation which are highly active at a low loading of the active component, it seems appropriate to examine potentialities of improving the activity of the honeycomb monolith as a whole. The way to do this is through the optimal longitudinal distribution of the active component. It is well known that improved catalyst performance can be achieved using a non-uniform catalyst activity distribution within a pellet [4]. On the other hand, the problem of the influence of longitudinal non-uniform catalyst distribution was not studied properly, only several papers dealt with it. The case of parabolic catalyst distribution for CO oxidation was studied elsewhere [5]. A considerable improvement of CO conversion was shown possible under certain conditions due to the proper choice of the active component distribution at some fixed amount of it. It was shown for the reaction of methane oxidation [6] that non-uniform catalyst distributions have the potential to achieve lower thermal stresses. However, there were observed only minor changes in the methane conversion with all the distribution modes under study. Therefore, searching for the distribution parameters, which would increase conversion, is of interest. The present work was aimed at comparison of various longitudinal active component distributions in honeycomb monolithic catalysts in order to improve the efficiency for CO oxidation.

2. Mathematical formulation of the problem

Determination of the optimal longitudinal distribution of the active component is a new problem. Therefore, it is important to identify essential and inessential factors. So the reactor model is based on the most general physical concepts, which are described by a simple mathematical model. Complication of the model, in particular its three-dimensional realization, must not alter the principal conclusions. At the same time, more complicated model calculations do not

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Nomenclature

c	gas-phase concentration of CO (molar fraction)
c_{O_2}	oxygen concentration (molar fraction)
C_p	molar heat capacity ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
c_s	concentration of CO on the monolith surface (molar fraction)
D	CO diffusion coefficient in air ($\mathrm{m^2\,s^{-1}}$)
d_H	hydraulic diameter of a channel (m)
E_1	activation energies ($\mathrm{J\,mol^{-1}}$)
$f(\xi)$	function describing Pt distribution along the bed length
$f_n(\xi)$	power function of zero, first, second or third order used to construct a non-uniform longitudinal distribution of Pt
ΔH	heat of reaction ($\mathrm{J\,mol^{-1}}$)
ΔH_{ads}	adsorption energy ($\mathrm{J\,mol^{-1}}$)
k_A	adsorption equilibrium constant (dimensionless)
k_1	reaction rate constant ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
l	coordinate along monolith length (m)
L	monolith length (m)
ΔM_{Pt}	relative platinum amount decrease due to the non-uniform distribution
Pr	Prandtl number; used $Pr = 0.7$
$r(\xi)$	reaction rate at the non-uniform platinum distribution ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
R_g	gas constant ($8.314\,\mathrm{J\,mol^{-1}\,K^{-1}}$)
r_u	reaction rate ($\mathrm{mol\,m^{-2}\,s^{-1}}$)
$Re = u_C d_H/\nu$	Reynolds number
S	catalytic surface area per unit reactor volume ($\mathrm{m^{-1}}$)
$Sc = \nu/D$	Schmidt number
T	gas temperature (K)
$u_C = u/\varepsilon$	gas flow rate in the monolith channel under operation conditions ($\mathrm{m\,s^{-1}}$)
u_0	superficial gas flow rate at normal conditions ($\mathrm{m\,s^{-1}}$)
$x(\xi)$	conversion of CO
$x_1 = x(1)$	outlet CO conversion
$Z_C = l/(Re\,Sc\,d_H)$	dimensionless mass channel length
$Z_T = l/(Re\,Pr\,d_H)$	dimensionless thermal channel length

Greek letters

$\alpha = Nu(Z_T)\lambda_f/d_H$	gas–solid heat transfer coefficient ($\mathrm{W\,m^{-2}\,K^{-1}}$)
$\beta = Sh(Z_C)D/d_H$	gas–solid mass transfer coefficient ($\mathrm{m\,s^{-1}}$)
ε	monolith porosity
θ	catalyst temperature (K)
λ_f	heat conductivity of gas ($\mathrm{W\,m^{-1}\,K^{-1}}$)
λ_S	monolith heat conductivity ($\mathrm{W\,m^{-1}\,K^{-1}}$)
ν	kinematic viscosity ($\mathrm{m^2\,s^{-1}}$)
ξ	coordinate along monolith length (dimensionless)
ξ_0	boundary of the monolith region with distributed active component
$\Delta\xi_{Pt}$	length of the monolith region with distributed active component
ρ	total concentration under operation conditions ($\mathrm{mol\,m^{-3}}$)
ρ_0	total concentration at normal conditions ($\mathrm{mol\,m^{-3}}$)

produce anything new but make the calculations more laborious because comparison of various types of distributions usually implies computing of a huge number of versions, unless the analytic solution of the optimization problem is available, and complicates interpretation of the results obtained.

Therefore, a simple, lumped one-dimensional model was used in the present work for calculation of the process of CO oxidation in a honeycomb monolith. The model described the process in an isolated channel of the monolith, conditions being assumed identical in each channel.

The stationary mathematical model used in the present study involves the following processes:

1. convective heat and mass transfer in gas phase;
2. heat conduction in solid phase;
3. heat and mass transfer between the phases.

The model implies that the reaction of CO oxidation occurs on the catalyst surface, the pore-diffusion resistance being not taken into account.

The effects caused by the gas heat conductivity and diffusion along the channel axis were assumed negligible. Physical properties of the gas (density, thermal capacity, heat conductivity, gas viscosity) were assumed to depend on the gas temperature within the channel of the monolith. The respective values were taken constant for the whole monolith and determined at the mean temperature of the flowing gas (that was allowed at low concentrations of CO and, hence, at little variations in the gas temperature along the channel axis). Temperature dependence of the gas properties was taken into consideration in the conventional way [7]. The assumptions above are commonly accepted and used for development of similar models (see, for example, Ref. [8]).

Based on these assumptions, equations of heat and mass balance will be written as follows:

$$(1-\varepsilon)\lambda_{\mathrm{s}}\frac{\mathrm{d}^2\theta}{\mathrm{d}l^2} - S\alpha(\theta - T) + S\Delta H r(c_{\mathrm{s}},\theta) = 0, \tag{1}$$

$$u_0\rho_0 C_p\frac{\mathrm{d}T}{\mathrm{d}l} - S\alpha(\theta - T) = 0, \tag{2}$$

$$u_0\rho_0\frac{\mathrm{d}c}{\mathrm{d}l} + S\beta\rho(c - c_{\mathrm{s}}) = 0, \tag{3}$$

$$\beta\rho(c - c_{\mathrm{s}}) = r(c_{\mathrm{s}},\theta). \tag{4}$$

Boundary conditions:

$$l = 0: \quad c = c_0, \quad T = T_0, \quad \frac{\mathrm{d}\theta}{\mathrm{d}l} = 0;$$

$$l = L: \quad \frac{\mathrm{d}\theta}{\mathrm{d}l} = 0. \tag{5}$$

Heat and mass transfer coefficients were calculated using interpolation formulae derived by the authors of Ref. [9] to determine local Nusselt (*Nu*) and Sherwood (*Sh*) numbers. These formulae allow thermal and hydrodynamic characteristics of the entrance region and the influence of the duct geometry to be taken into consideration:

$$Nu = Nu_\infty + 8.827(1000Z_{\mathrm{T}})^{-0.545}\exp(-48.2Z_{\mathrm{T}}), \tag{6}$$

$$Sh = Sh_\infty + 8.827(1000Z_{\mathrm{C}})^{-0.545}\exp(-48.2Z_{\mathrm{C}}). \tag{7}$$

For square duct $Nu_\infty = Sh_\infty = 2.977$.

A numerical algorithm was developed using finite-difference methods for the calculations according to the models (1)–(5). An irregular grid was built for spatial variable $l \in [0, L]$ (or for dimensionless variable $\xi = l/L, \xi \in [0, 1]$), the grid being finer at the inlet of the monolith (for uniform length distribution of platinum) or in the reaction zone (for the non-uniform distribution). Eq. (1) was approximated using a balance difference scheme of second order of accuracy, and the obtained algebraic system was solved by the factorization method. The Euler schemes of second order of accuracy were used for numerical solution of Eqs. (2)–(4). Eqs. (3) and (4) were solved simultaneously, and the non-linear algebraic systems obtained by the difference approximation of these equations was solved by the Newton method. Since the system (1)–(4) is non-linear, the iteration process was provided in the algorithm after calculation of the numerical solution of each of Eqs. (1)–(4) for refinement of the solution of the whole system.

Eqs. (1) and (4) comprise the expression for the rate, $r(c_{\mathrm{s}}, \theta)$, of CO oxidation over the monolith catalyst, the rate being dependent on the platinum distribution along the monolith length, which is given by function $f(\xi)$. To describe the reaction rate at a uniform platinum distribution $f_{\mathrm{u}}(\xi)\equiv 1$, bimolecular Langmuir–Hinshelwood kinetic equation with reaction rate constants determined in [3,10] was used:

$$r_{\mathrm{u}}(c_{\mathrm{s}},\theta) = \frac{k_1\exp(-E_1/R_{\mathrm{g}}\theta)c_{\mathrm{s}}c_{\mathrm{O}_2}}{(1 + k_{\mathrm{A}}\exp(\Delta H_{\mathrm{ads}}/R_{\mathrm{g}}\theta)c_{\mathrm{s}})^2}. \tag{8}$$

The kinetic model was based on the commonly accepted assumption [1] of the linear dependence of the rate of CO oxidation on the platinum concentration $f(\xi)$, i.e. $r(c_{\mathrm{s}},\theta) = f(\xi)r_{\mathrm{u}}(c_{\mathrm{s}},\theta)$. The effect of the non-uniform axial active component distribution on the overall CO conversion could be determined by solving the set of Eqs. (1)–(5) for various preset activity distributions, $f(\xi)$, along the bed length.

There were two problems that needed addressing in this study: firstly, how to boost overall CO conversion by concentrating Pt in the right places while utilizing the same amount of Pt, secondly, how to make use of Pt distribution to minimize the amount of Pt in the monolith while maintaining high overall conversion.

Several types of power functions describing active component distribution were used for numerical analysis. The shape of these dependencies implied that there existed a preferable region of concentrating the active component at the inlet, middle or outlet fragment.

Various platinum distribution profiles along the monolith length as a function of dimensionless length coordinate ξ are shown in Fig. 1. The platinum distribution along the monolith length is given by function $f(\xi) = A_{\mathrm{n}}f_{\mathrm{n}}(\xi)$, where $f_{\mathrm{n}}(\xi)$ is some power function of zero, first, second or third order. Parameter A_{n} is the normalizing factor determined from the condition of platinum mass conservation, because for resolving the problem of improvement of CO conversion due to axially non-uniform platinum distribution, the total platinum content was taken constant:

$$\int_0^1 A_{\mathrm{n}}f_{\mathrm{n}}(\xi)\,\mathrm{d}\xi = 1 \tag{9}$$

The value of ξ_0 (where ξ_0 is a fixed value determining the length of the platinum-containing monolith fragment) was

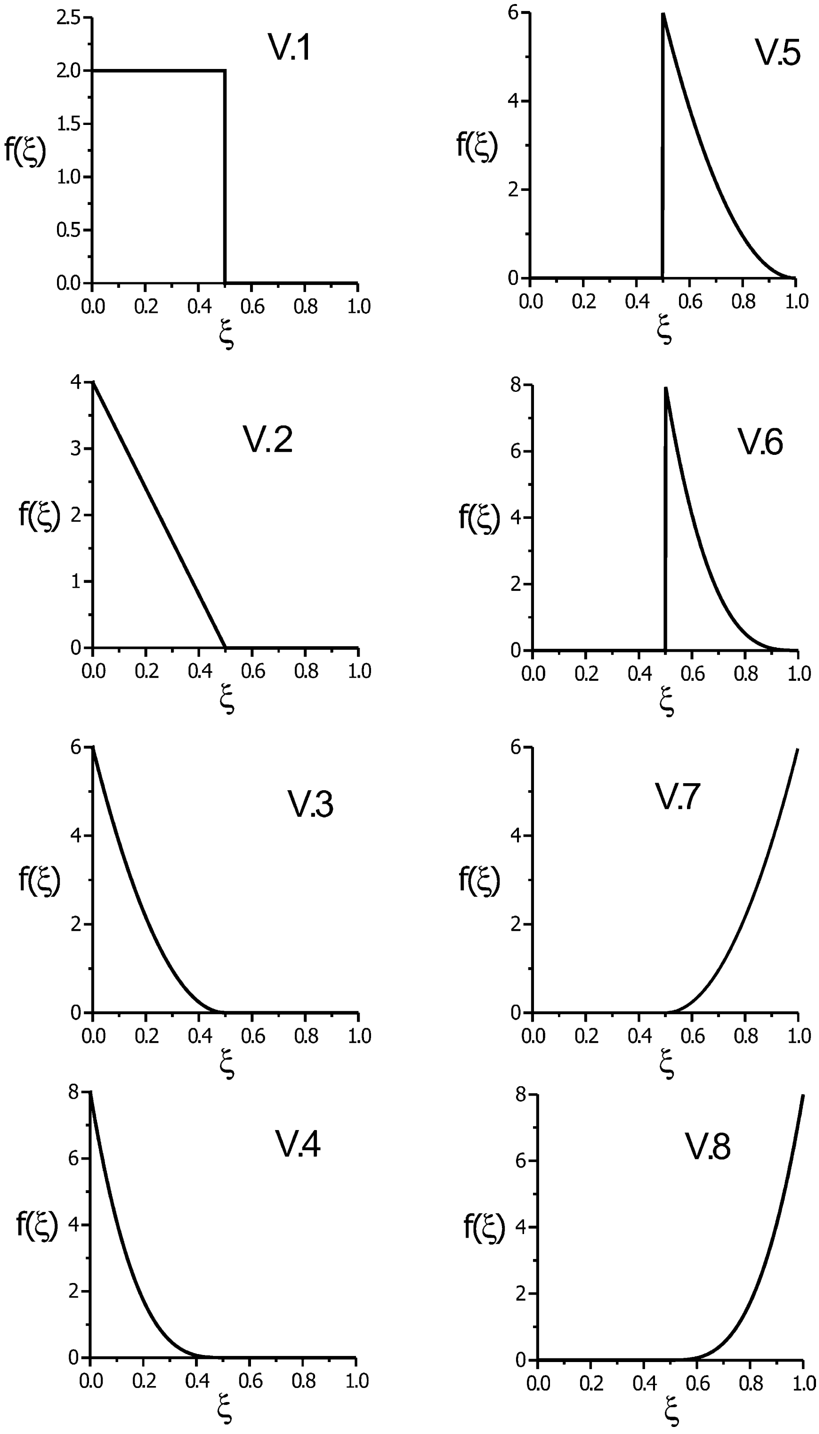

Fig. 1. Longitudinal platinum distribution variants: V.0: $f_{\mathrm{u}}(\xi) = 1$ (uniform); V.1: $f(\xi) = A$ for $\xi \le \xi_0$, $f(\xi) = 0$ for $\xi > \xi_0$; V.2: $f(\xi) = A(\xi - \xi_0)$ for $\xi \le \xi_0$, $f(\xi) = 0$ for $\xi > \xi_0$; V.3: $f(\xi) = A(\xi - \xi_0)^2$ for $\xi \le \xi_0$, $f(\xi) = 0$ for $\xi > \xi_0$; V.4: $f(\xi) = A(\xi - \xi_0)^3$ for $\xi \le \xi_0$, $f(\xi) = 0$ for $\xi > \xi_0$; V.5: $f(\xi) = A(\xi - 1)^2$ for $\xi \ge \xi_0$, $f(\xi) = 0$ for $\xi < \xi_0$; V.6: $f(\xi) = A(\xi - 1)^3$ for $\xi \ge \xi_0$, $f(\xi) = 0$ for $\xi < \xi_0$; V.7: $f(\xi) = A(\xi - \xi_0)^2$ for $\xi \ge \xi_0$, $f(\xi) = 0$ for $\xi < \xi_0$; V.8: $f(\xi) = A(\xi - \xi_0)^3$ for $\xi \ge \xi_0$, $f(\xi) = 0$ for $\xi < \xi_0$.

varied to provide the level of concentration of the active component.

The polynomial degree increment results in an increase in the total concentration of the active component within a narrow region. Different modes of platinum distribution with the active component concentrated within the initial fragment of the monolith are shown in Fig. 1 (V.1–V.4). $\xi_0 = 0.5$ here is the dimensionless length of the monolith part comprising platinum (notice that the uniform axial Pt distribution corresponds to V.1 at $\xi_0 = 1$; this kind of distribution is referred to as V.0 below). The value $\xi_0 = 0.5$ in Fig. 1 (V.5–V.8) is the catalyst-free fragment of the monolith, all platinum being concentrated at the rest part of the monolith. The dimensionless length of a platinum-containing monolith fragment is hereinafter symbolized as $\Delta\xi_{\mathrm{Pt}}$.

At high conversions of CO, the aim was to minimize the platinum content. To resolve the problem, the platinum distribution along the monolith length is given by function $f(\xi) = B_{\mathrm{n}} f_{\mathrm{n}}(\xi)$, where $f_{\mathrm{n}}(\xi)$ is the same power function of zero, first, second or third order. A probable decrease in the amount of platinum, ΔM_{Pt}, due to the non-uniform distribution was determined so as not to lower the degree of cleaning from CO observed at the uniform distribution. Formula

$$\Delta M_{\mathrm{Pt}} = 1 - \int_0^1 B_{\mathrm{n}} f_{\mathrm{n}}(\xi)\,\mathrm{d}\xi \qquad (10)$$

was used for calculation of ΔM_{Pt}, where B_{n} was determined to provide the conversion at the given distribution as equal to that at the uniform distribution. Saving in Pt will be achieved if $B_{\mathrm{n}} < A_{\mathrm{n}}$.

In the next part it will be shown how replacement of uniform by non-uniform platinum distribution along the monolith length affects the efficiency of catalytic monolith operation.

3. Results of mathematical modeling

Computation of the CO oxidation process was performed for the following conditions, which were typical for burning of the automotive engines exhaust gases (Table 1).

Calculations are performed for different (low, moderate and high) conversions of CO achieved by varying the inlet temperature of the flowing gas. Figs. 2 and 3 demonstrate the influence of the platinum distribution on the reaction rate, monolith temperature and CO conversion at various inlet gas flow temperatures. For the calculations illustrated in Fig. 2, the inlet gas temperature was chosen below the ignition obtained for the uniform platinum distribution. For the data in Fig. 3, the inlet temperature is chosen above the ignition point. Notice that the temperature and concentration profiles for the two cases are essentially different at the uniform platinum distribution but behave the same way at the non-uniform longitudinal distribution. That is because ignition is observed at a lower inlet temperature in the case of non-uniformly distributed platinum. The reaction rate increases with increasing platinum concentration in a narrow fragment of the monolith length that results in ignition at low inlet gas temperatures.

Table 1
Monolith characteristics and operation conditions used for calculations (after Ref. [1])

Monolith length, L (cm)	10
Channel size (square section) (mm)	0.94
Wall thickness (mm)	0.1
Flow rate of gas to be cleaned, u_0 ($\mathrm{m\,s^{-1}}$)	0.56
Inlet concentration of CO, C_0	0.005
Oxygen concentration, $C_{\mathrm{O_2}}$	0.1
Temperature of inlet gas flow, T_0 (°C)	180–190
Catalytic surface area per unit reactor volume, S ($\mathrm{m^{-1}}$)	3476.33
Void fraction, ε	0.817
Monolith heat conductivity, λ_{s} ($\mathrm{W\,m^{-1}\,K^{-1}}$)	1.68
Reaction rate constants	
k_1 ($\mathrm{mol\,m^{-2}\,s^{-1}}$)	2.01×10^{12}
k_{A}	65.5
E_1 ($\mathrm{J\,mol^{-1}}$)	104756
ΔH_{ads} ($\mathrm{J\,mol^{-1}}$)	7990

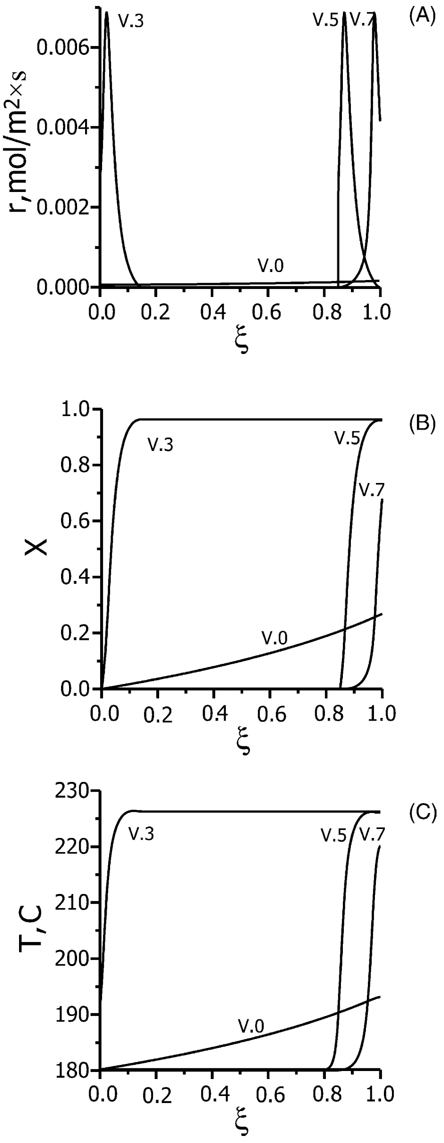

Fig. 2. Reaction rate (A), CO conversion (B), catalyst temperature (C) vs. monolith length. $T_0 = 180\,^{\circ}\mathrm{C}$ and $\Delta\xi_{\mathrm{Pt}} = 0.15$. Legend as in Fig. 1.

Results of calculation of CO conversion at different inlet temperatures depending on the longitudinal distribution of platinum are summarized in Figs. 4–8.

At low conversions of CO, the problem under study was to boost the conversion at the monolith outlet. The calculated

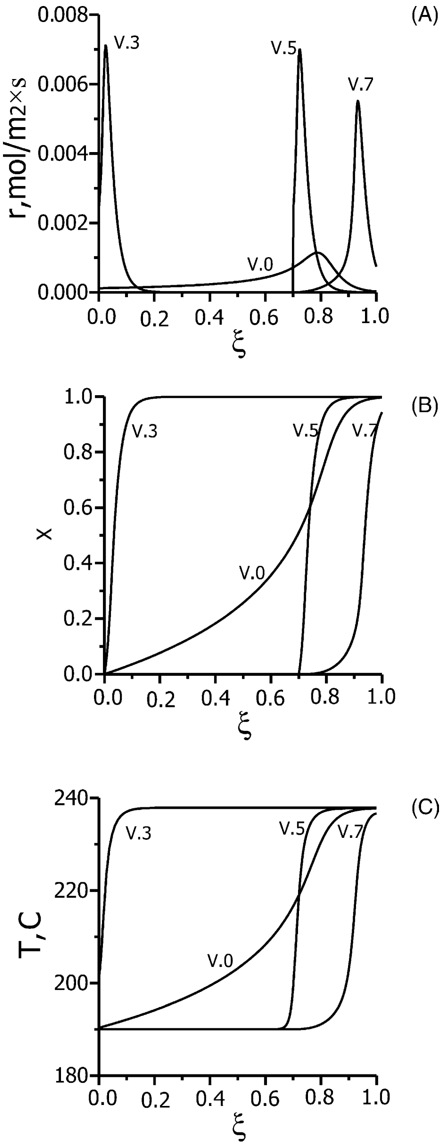

Fig. 3. Reaction rate (A), CO conversion (B), catalyst temperature (C) vs. monolith length. $T_0 = 190\,^{\circ}\mathrm{C}$ and $\Delta\xi_{\mathrm{Pt}} = 0.3$. Legend as in Fig. 1.

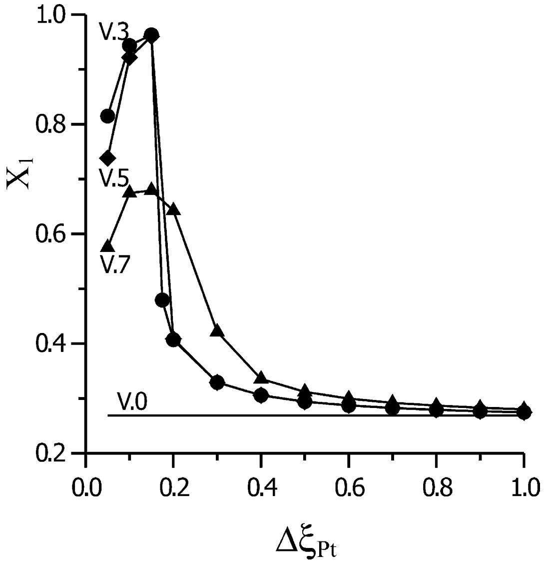

Fig. 4. Outlet CO conversion vs. length of the platinum-containing monolith part $\Delta\xi_{\mathrm{Pt}}$. Inlet gas flow temperature $T_0 = 180\,^{\circ}\mathrm{C}$ and $x_1 = 0.268$ at the uniform distribution. The platinum distribution along the monolith length is given by second-order power functions with the exception of V.0 when function is constant. Legend as in Fig. 1.

data given in Figs. 4 and 5 (for the inlet gas temperature $T_0 = 180\,^{\circ}\mathrm{C}$) demonstrate the influence of non-uniform longitudinal platinum distribution on the conversion.

Fig. 4 shows the effect on the outlet CO conversion of concentrating the total amount of Pt using the second-order distribution functions at the inlet, middle and outlet of the monolith and compares it to the uniform distribution.

Analysis of the curves (Fig. 4) reveals that replacement of the uniform by non-uniform platinum longitudinal distribution always leads to an increase in the CO conversion irrespectively of the concentration and of the location of fragment where platinum is concentrated. At the same time, there is a maximum in the dependence of CO conversion on the fragment length $\Delta\xi_{\mathrm{Pt}}$. The choice of the length fragment for platinum concentrating also influences on the CO conversion. Preferable is the platinum concentration in the outlet fragment up to the length of $\Delta\xi_{\mathrm{Pt}} > 0.2$ (V.7). However, the highest conversion may be achieved when all platinum is concentrated in a narrow fragment in the monolith entrance region ($\Delta\xi_{\mathrm{Pt}} \cong 0.2$) (V.3).

At low gas temperatures the influence of the platinum-containing monolith part length is the most essential when platinum is concentrated in an inlet monolith fragment (Fig. 4). Fig. 5 shows the effect of the distribution shape (zero to third order) on the outlet CO conversion, when the total amount of Pt is located at the monolith inlet. From calculations for the inlet gas temperature $T_0 = 180\,^{\circ}\mathrm{C}$, the outlet CO conversion can be improved from $x_1 = 0.268$ (at uniform distribution, see V.0) to $x_1 = 0.973$ (distribution is described by cubic dependence, see V.4) owing to concentrating platinum at the inlet region of the catalytic monolith. The shape of the axial platinum distribution curves is a more important factor when the active component is concentrated within a small fragment of the monolith, the efficiency being increased from the stepwise distribution (V.1) to the cubic distribution (V.4). In this case the optimal fragment length $\Delta\xi_{\mathrm{Pt}}$ providing the highest possible conversion of CO exists for each distribution variant under consideration.

As the inlet temperature is elevated, the influence of platinum concentrating on the increase in the CO conversion appears less significant. To illustrate this, let us consider Fig. 6 where the conversion of CO is plotted as a function of $\Delta\xi_{\mathrm{Pt}}$ for different types of the active component distribution for the inlet gas flow temperature $T_0 = 186\,^{\circ}\mathrm{C}$. In this case the outlet CO conversion was increased from 0.686 at the uniform distribution to 0.997 at the cubic distribution (V.4). At a higher inlet temperature, platinum concentrating in a certain monolith fragments also causes an increase

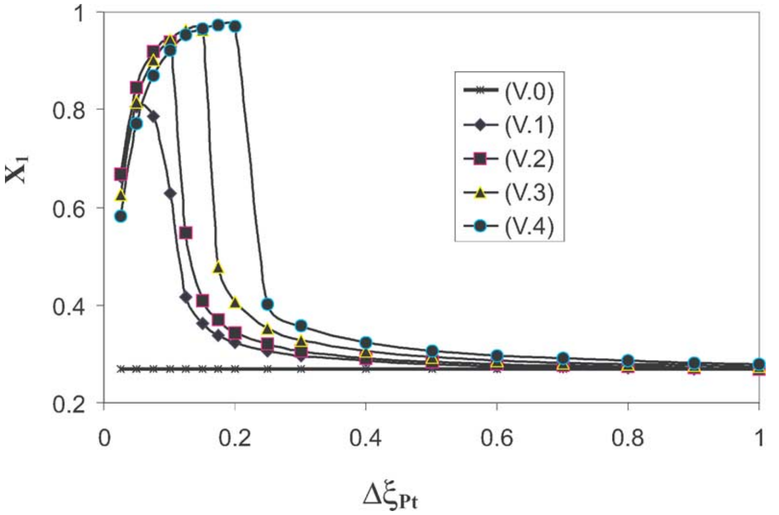

Fig. 5. Outlet CO conversion vs. length of the platinum-containing monolith part $\Delta\xi_{Pt}$. Inlet gas flow temperature $T_0 = 180\,^\circ C$ and $x_1 = 0.268$ at the uniform distribution. Platinum is allocated at the inlet of the monolith, $\xi_0 = \Delta\xi_{Pt}$, platinum distribution along the monolith length is given by zero-, first-, second- and third-order power functions. Legend as in Fig. 1.

in the CO conversion (Fig. 6) in comparison to that at the uniform distribution, the highest conversion being achieved when all amount of platinum is concentrated in the inlet fragment (V.4). At the same time, when all amount of platinum is concentrated in the outlet fragment (V.8) of practically any length $\Delta\xi_{Pt}$, the conversion of CO is considerably lower than the conversion observed with platinum concentrated in a middle or inlet monolith fragment. Notice that at high inlet temperature (higher than the ignition temperature) CO conversion is lower if Pt is concentrated at the monolith outlet (in accordance to V.7 and V.8) but not distributed uniformly.

If the CO conversion is high enough at the uniform platinum distribution, the problem of minimization of a total platinum amount is of importance rather than the problem of boosting the outlet CO conversion. Let us consider the solution of this problem in terms of the non-uniform platinum distribution along the monolith length provided that the outlet CO conversion is not lower than that at the uniform distribution. In our work the problem was resolved for

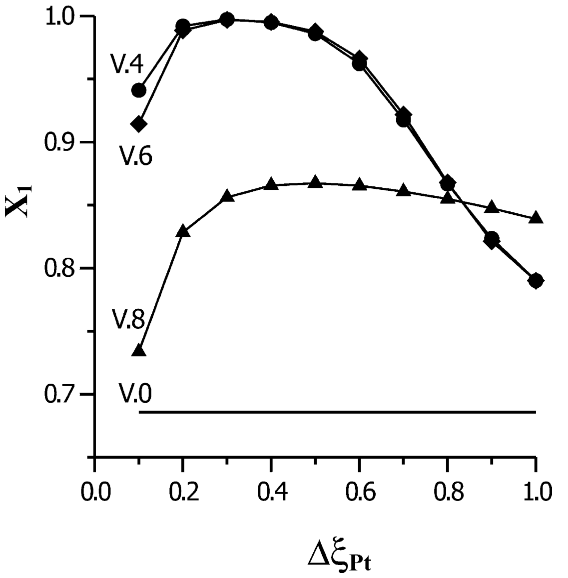

Fig. 6. Outlet CO conversion vs. length of the platinum-containing monolith part $\Delta\xi_{Pt}$. Inlet gas flow temperature $T_0 = 186\,^\circ C$ and $x_1 = 0.686$ at the uniform distribution. The platinum distribution along the monolith length is given by third-order power functions. Legend as in Fig. 1.

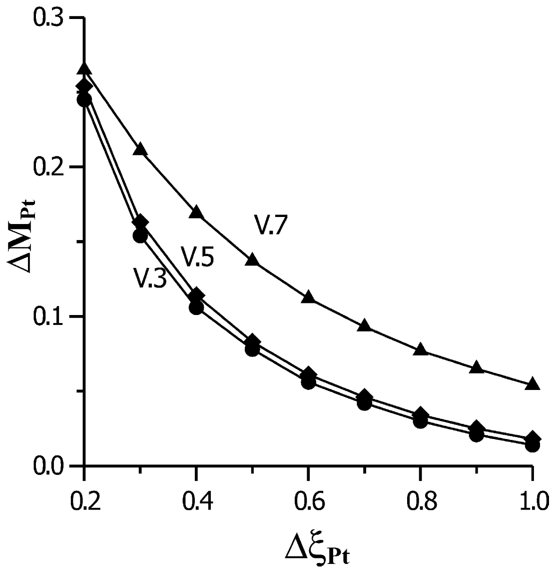

Fig. 7. Decrease in the amount of platinum ΔM_{Pt} vs. length of the platinum-containing monolith part $\Delta\xi_{Pt}$. Inlet gas flow temperature $T_0 = 186\,^\circ C$ and $x_1 = 0.686$ at the uniform distribution. The platinum distribution along the monolith length is given by second-order power functions. Legend as in Fig. 1.

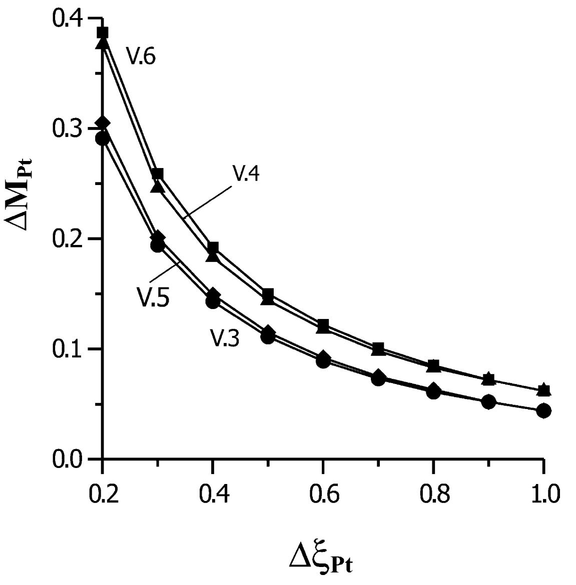

Fig. 8. Decrease in the amount of platinum ΔM_{Pt} vs. length of the platinum-containing monolith part $\Delta\xi_{\mathrm{Pt}}$. Inlet gas flow temperature $T_0 = 188\,^\circ\mathrm{C}$ and $x_1 = 0.955$ at the uniform distribution. The platinum distribution along the monolith length is given by second- and third-order power functions. Legend as in Fig. 1.

two values of the inlet gas temperature: $T_0 = 186\,^\circ\mathrm{C}$ (Fig. 7) and $T_0 = 188\,^\circ\mathrm{C}$ (Fig. 8).

Dependencies in Fig. 7 demonstrate a possibility of diminishing platinum loading in the honeycomb monolith at various platinum distribution at the inlet gas temperature $T_0 = 186\,^\circ\mathrm{C}$ corresponding to the moderate conversion of CO ($x_1 = 0.686$). In this case a total platinum amount can be decreased using any type of the non-uniform longitudinal distribution under consideration. As the fragment length $\Delta\xi_{\mathrm{Pt}}$ decreases, the potential saving in platinum increases, the most essential effect being observed when all platinum is concentrated in a narrow fragment adjacent to the monolith outlet (V.7). At $\Delta\xi_{\mathrm{Pt}} = 0.2$, the total platinum loading may be 25% decreased. The most ineffective is to concentrate Pt in the inlet fragment. Higher degrees of platinum concentration are not effective, either.

At elevated inlet gas temperature ($T_0 = 188\,^\circ\mathrm{C}$), the high outlet CO conversion ($x_1 = 0.955$) is observed at the uniform longitudinal platinum distribution. When so, even more saving in platinum can be achieved due to the use of the non-uniform distribution (Fig. 8). However, the CO conversion appears lower for V.7- and V.8-type distribution than for the uniform distribution of the same amount of platinum. The data illustrated in Fig. 8 demonstrate that the preferable version is concentrating of platinum at some distance from the inlet (V.6, Fig. 8). In this case the platinum content may decreased by almost 40% at the preserved high conversion of CO. Again, similar to the case of low inlet gas flow temperature (Fig. 7), ΔM_{Pt} increases with a decrease of the Pt-occupied fragment length (i.e. with an increase of the platinum concentration degree in this fragment) to a certain limit and the further fragment shortening to $\Delta\xi_{\mathrm{Pt}} < 0.2$ leads to lower ΔM_{Pt}. Moreover, the conversion of CO becomes lower at concentrating platinum in a very narrow fragment in the entrance or middle part of the monolith than at the uniform longitudinal distribution of the same Pt amount.

4. Discussion of calculated results

The calculated results on CO oxidation demonstrate that application of a non-uniform longitudinal platinum distribution may lead in many cases to more effective operation of the monolith as a whole.

At temperatures lower than the ignition point, the ignition conditions may be improved due to redistribution of a fixed amount of the catalyst along the monolith length. That occurs when Pt is concentrated in a certain fragment of the catalytic bed length (Fig. 2), the localization of the concentrated fragment (entrance, middle or end of the monolith) being of practically no importance if the fragment length is not very short. In this case the outlet CO conversion appears considerably higher than that observed at the uniform distribution of the identical amount of platinum (Figs. 4 and 5). In addition, if the ratio of the reaction rate and diffusion limitations varies along the catalyst bed, then the efficiencies of active component unit (Pt) differ in individual monolith fragments. The efficiency of the monolith operation as a whole can increase when a part of Pt is transferred from the low-effective region to the high-effective region. In the case of negligible mass transfer resistance under isothermal conditions, the reaction rate is apparently determined by the total active component weight only.

The results obtained by calculations demonstrate that for each distribution type there is an optimal length of the monolith fragment occupied by platinum, where the highest conversion is achieved. This is accounted for by the fact that, at temperatures higher than the ignition point, the conversions depends only on the rate of reactant feeding to the catalyst surface. If so, the gas-phase conversion is determined by the length of the fragment occupied by Pt. The further increase in the Pt concentration leads to a decrease in the conversion due to shortening of the reaction zone. Taking into account higher coefficients of heat and mass transfer in the monolith entrance region (see dependencies (6) and (7)), it seems preferable to concentrate platinum nearby the entrance.

The calculations reveal that the stepwise Pt distribution is not the best way to maximize conversion. The shape of the axial platinum distribution curves is a more important factor when all the active component is concentrated within a small fragment of the monolith (Fig. 5), the efficiency being increased from the stepwise distribution (V.1) to the cubic distribution (V.4). The non-uniform distribution given by a higher-order polynomial seems the best in many cases.

The possibility of the inlet temperature reduction at the preserved efficiency of CO oxidation is of particular importance. With the uniformly distributed active component, the conversion of CO equal to 0.95–0.96 is attained at the inlet gas flow temperature $T_0 = 188\,^\circ\mathrm{C}$. As to the case of non-uniform distribution, the conversion equal to 0.973 is observed at $T_0 = 180\,^\circ\mathrm{C}$ (see V.4, Fig. 5). Thus, the inlet temperature can be reduced by 8 °C at the same degree of cleaning.

Since the active component of the catalyst (platinum) is highly expensive, it seems appropriate to examine if it is possible to decrease the platinum loading in the honeycomb monolith due to its non-uniform distribution through the monolith length at the preserved conversion of CO.

At high temperatures (ignition occurs in the monolith entrance), platinum concentrating may have a detrimental effect on the conversion in comparison to that at the uniform distribution. However, this is also the case when the platinum redistribution may either improve the outlet CO conversion (Fig. 6) or minimize platinum loading at the same conversion (Figs. 7 and 8).

In view of non-linear kinetics of CO oxidation, when the reactant is strongly adsorbed on the catalyst, it is preferable to allocate the active component at the region of low CO concentrations (i.e. at the monolith output). The results obtained support the conclusion. It was shown that rather high conversion of CO at the uniform distribution can be preserved at a lower loading of platinum distributed in non-uniform manner. Figs. 7 and 8 can be used for the determination of preferable regions of the monolith for platinum concentrating. It is found that the most remarkable changes in the platinum content at relatively low conversions ($x_1 = 0.686$) are observed with platinum allocated at the regions adjacent to the monolith outlet (see curves V.7 in Fig. 7). The platinum concentrating at the inlet regions is only preferable at $\xi(\mathrm{Pt}) < 0.2$. An estimated decrease in the platinum content is 20–25%. As the inlet temperature and, consequently, the CO conversion increases (Fig. 8), the preferable version is concentrating of platinum at some distance from the inlet (V.6, Fig. 8). In this case the platinum content may be decreased by almost 40% at the preserved high conversion of CO.

There is an interesting question, in what cases the platinum concentrating may cause violation to the linear dependence of reaction rate on the platinum concentration.

There may be two cases of violation of the assumption about the linear dependence of reaction rate on active component concentration. First, properties of the support or active component, e.g. dispersion of platinum, can alter as the active component concentration increases. As a result, the activity per unit mass will decrease with increasing concentration. However, these changes in the catalyst properties relate more to the art of catalyst preparation. The currently available methods for platinum catalyst preparation allow the dependence of activity on active component concentration to be close to linear in wide enough range of active component concentrations. It is experimentally shown [11] for the platinum concentration ranging between 0.25 and 2% that the dependence of the rate of CO oxidation on platinum concentration can be expressed in the form of power dependence with exponent equal to 0.9.

Second, an increase in the platinum concentration brings to a higher pore-diffusion resistance thus decreasing the catalyst effectiveness factor. It is shown [3] that the effectiveness factor for Langmuir–Hinshelwood kinetics under non-isothermal conditions is determined by heat and mass Biot numbers and by Thiele modulus. The calculations [3] refer to a spherical grain but the estimations are thought to be approximately applicable for monolith in consideration of the characteristic thickness of the supported active component layer as equal to particle half-diameter.

With the process conditions under consideration (inlet temperatures and concentrations) and average values of washcoat equal to 0.05 mm, Thiele modulus = 0.026, mass Biot numbers = 0.88 and heat Biot numbers = 0.158 can be obtained using the reaction rate per unit catalyst volume [3] and the relationship of the effective CO diffusion inside the grain and the gas-phase diffusion [12]. It is shown [3] that the effectiveness factor can be considered equal to 1 for these Biot numbers and all values of Thiele modulus less than 0.1.

The active component concentration can be increased by two methods, viz. by increasing washcoat thickness or by increasing the platinum concentration in the washcoat. In the former case the Thiele modulus increases in direct proportion to the washcoat thickness, while in the latter case it is proportional to square root of the active component concentration. In the case under consideration, for either method in the range of four-fold increment of the Thiele modulus the effectiveness factor remains close to 1. On further increasing concentration up to Thiele modulus equal to 0.12–0.6 the effectiveness factor will be higher than 1 due to specific features of the Langmuir–Hinshelwood kinetics. Thus, in the range of parameters under consideration in the present paper, platinum concentrating in a narrow fragment of the monolith does not result in a considerable diffusion limitation.

5. Conclusions

In the present work it was shown that the non-uniform active component distribution is in many cases more effective (regarding economic aspects and improvement of the conversion) than the uniform distribution. The reaction of CO oxidation over a Pt-containing monolith catalyst is used as an example.

The following problems can be resolved due to the non-uniform platinum distribution through the length of honeycomb monoliths: improvement of CO conversion at the monolith outlet (at low inlet gas temperatures) or minimization of the total platinum loading at maintaining the conversion not lower than the conversion attained at the uniform distribution (at high inlet gas temperatures). To provide a decrease in the inlet gas flow temperature at preserved CO conversion needs platinum concentrating within the inlet region of the monolith, the maximal conversion being reached at a certain length of this region. The presented examples demonstrate possibility of lowering the inlet temperature by ca. 10 °C. Total platinum loading can be reduced if platinum is concentrated at the regions adjacent to the monolith outlet. As the inlet temperature increases, the maximal platinum-loaded region should be moved towards the inlet of the gas flow. For the initial conditions considered in the present paper, a total reduction of loading in the honeycomb monolith (at the preserved degree of cleaning) can attain 20–40% of the initial amount of uniformly distributed platinum due to the non-uniform distribution.

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