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Kinetic instabilities and intra-thread diffusion limitations in CO oxidation reaction at Pt/fiber-glass catalysts

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Abstract

Experimental and mathematical simulation studies of CO oxidation reaction at Pt-based glass-fiber catalyst showed that reaction phenomena in fabric and threads of woven glass-fiber catalysts is rather complicated by transfer limitations, which may impose especially valuable influence on reactions with strongly non-linear kinetics. Such limitations are related to extra-thread and intra-thread heat and mass transfer. Additionally, in thin beds, consisting of one or few layers of woven catalyst, the significant role may be played by experimentally confirmed transient oscillations between CSTR and plug-flow regimes, therefore, the axial heat and mass dispersion is an important transfer factor for such beds as well.

Mathematical modelling of phenomena inside the catalyst thread on the basis of elaborated kinetic model showed possibility of existence of steady-state multiplicity as a self-sufficient result of intra-thread transfer limitations. In general, observed reaction rates at the catalyst thread and location of multiplicity region may depend upon many factors (thread diameter and porosity, surface CO concentration and temperature and even choice of reaction media balance gas), which should be taken into account for correct formulation of lab experimental procedure, interpretation of experimental data and process scale-up.

Keywords: Intra-thread diffusion; Pt/fiber-glass catalysts; CO oxidation reaction

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1. Introduction

Novel catalysts comprising noble metals (Pt and Pd), supported on fiber-glass (FG) woven support [1] have attained a lot of attention recently both from theoretical and applied points of view. Though the research of their catalytic properties is developing very fast, still there is a lack of understanding of heat/mass transfer processes in various packing of fibrous catalysts. Earlier non-trivial influence of external mass transfer limitations in woven catalyst packing was reported for SO_2 oxidation reaction [2]. Though these results were obtained in pilot plant tests with low accuracy level, nevertheless, it may be stated that diffusion limitations may influence significantly the efficiency of processes in fiber-glass beds.

The situation becomes especially complicated for reactions with strongly non-linear kinetics, such as CO oxidation by oxygen over noble-metal catalysts. Earlier studies of these reaction at Pt/FG [3] and Pd/FG [4] catalysts showed that reaction kinetics may be expressed by an equation with second-order inhibition term, being a source of kinetic instabilities (reaction rate hysteresis, oscillations, etc.). Such instabilities are generally typical for CSTR reactor, though they may be also observed in plug flow reactor under influence of external diffusion limitation factors [5].

2. Experiments

The Pt/FG catalysts (~0.01% mass Pt at high-silica glass fibers) were prepared by means of specially developed technique [1], providing positioning of platinum in thin subsurface layer of glass microfibers in metastabe ionic form. Geometrically, such catalysts represent themselves the glass-fiber threads, structured into woven fabric (Fig. 1). Every such thread, with external diameter of ~1 mm, is knitted from glass microfibers with typical diameter of 5–10 μm (Fig. 2).

The catalyst was tested in the experimental installation, using three types of reactor and catalyst arrangement (see Fig. 3). In type A and B the catalyst was used in form of separated fibers (looking like glass-wool), in type C—as a single-layer fragment of glass-fiber fabric, positioned perpendicular to the gas flow. Type A was supplied by flow recycling system. In all cases the catalyst was placed on the porous solid support made of foamed quartz.

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Nomenclature

C_{CO}, $C(r)$	concentration of CO (dimensionless = molar fractions)
D_{eff}	effective diffusivity coefficient (m^2/s)
D_{mol}	molecular diffusivity coefficient for CO in reaction media balance gas (m^2/s)
E_1	activation energy (kJ/mol)
E_2	inhibition term temperature dependence factor (kJ/mol)
k_1	kinetic rate constant (s^{-1}), $k_1 = k_{01}\exp(-E_1/R_cT)$
k_{01}	kinetic rate preexponent (s^{-1})
k_2	inhibition term constant (dimensionless), $k_2 = k_{02}\exp(E_2/R_cT)$
k_{02}	inhibition term preexponent (dimensionless)
Q	heat effect of CO oxidation reaction (kJ/mol)
r	coordinate along the thread radius (m)
R	thread external radius (m)
R_c	universal gas constant (kJ/mol/K)
T, $T(r)$	temperature (K)
w	kinetic function for CO oxidation rate (s^{-1})
W	observed rate of CO oxidation (s^{-1})

Greek letters

ε	thread porosity
λ_{eff}	effective coefficient of thread heat conductivity (kJ/m/s/K)
λ_g	coefficient of reaction media balance gas heat conductivity (kJ/m/s/K)
τ	residence time (s)

Subscripts and superscripts

in	value at the inlet of the reactor
out	value at the outlet of the reactor
surf	value at the thread surface

The reactors were placed inside the electrically heated furnace with temperature control system, providing maintenance of necessary temperature in the reactor with deviation not exceeding 0.1 °C. For accurate temperature measurements the thermocouples were positioned directly on the surface of catalyst.

The tests were performed with mixture of 900/500 ppmv CO, 10 vol.% oxygen and balance helium. Analysis of CO content in inlet and outlet gas was provided by gas chromatography.

Experiments in type A and B reactors with wool-alike catalyst were aimed to study the reaction kinetics under conditions of possibly minimized transfer limitations. Experiments with a piece of real catalytic fabric (type C) were made to reproduce the conditions of glass-fiber catalysts application in presence of transfer limitations on different scale levels (external transfer from gas flow bulk to catalyst thread surface and internal transfer inside the thread). Type A arrangement may be definitely identified as CSTR, while B was expected to behave like plug-flow reactor and probable behavior of C was not predominantly clear.

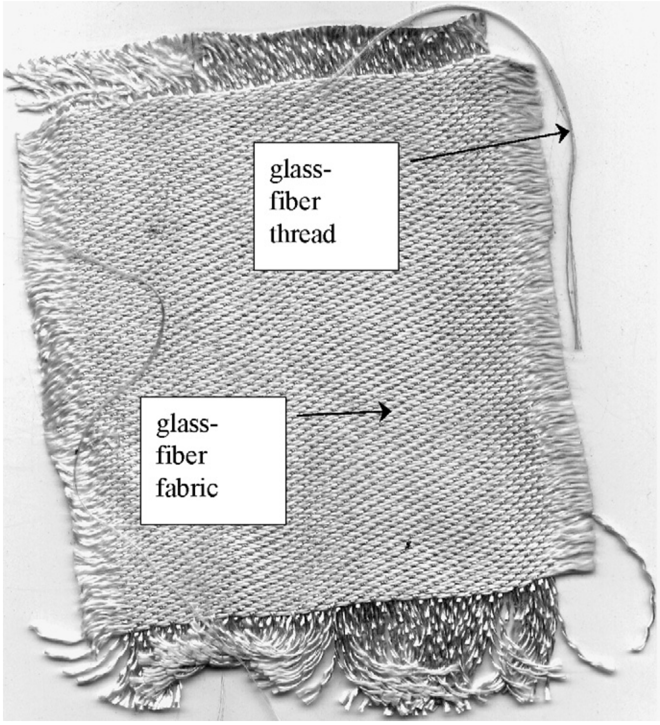

Fig. 1. Typical view of glass-fiber catalyst.

Some experimental results obtained are given in Fig. 4. It is seen that kinetic instabilities typical for noble-metal catalysts (such as reaction “light-off”, reaction rate hysteresis both with changing of temperature and residence time) are clearly observed for CSTR (Type A reactor). The well-known reason of these instabilities is strong non-linearity of kinetic equation with second-order inhibition term in combination with CSTR type equation for reactor.

The Type B reactor shows most likely plug-flow behavior with lower conversions and without conversion instability, which also is in good correspondence with theory.

The operation of disc (Type C) reactor appeared to be less predictable. For mixtures with higher CO content (900 ppmv) some experimental points are closer to Type A performance line, though some definitely belong to Type B curve. There-

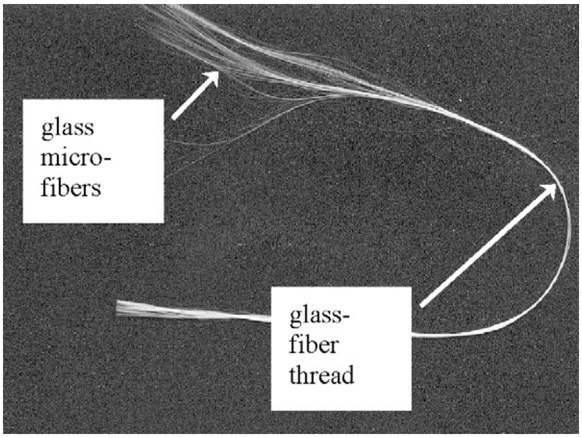

Fig. 2. Catalyst thread and microfibers.

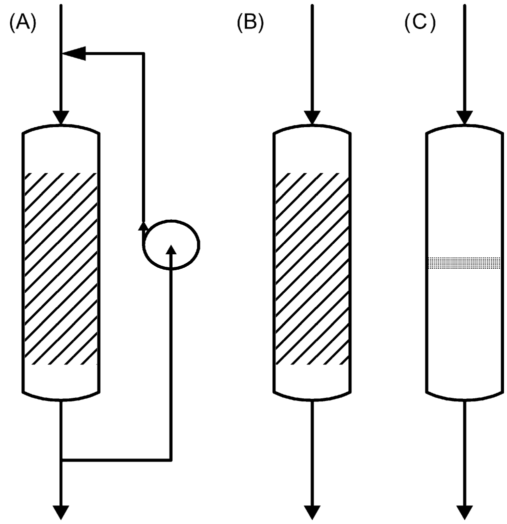

Fig. 3. Types of reactor and catalysts arrangement. (A) loop reactor with separate catalyst threads, (B) direct flow reactor with separate catalyst threads, (C) direct flow reactor with a single layer (disc) of woven catalyst fabric.

fore, it may be stated that kinetic instabilities in this case may be complicated by oscillations between CSTR/plug-flow reactor operation modes.

Type C operation is even more unstable in case of lower CO inlet concentration (500 ppmv). In this case the "light-off" is observed at lower temperature, but further increase of temperature does not lead to achievement of complete conversion and results in chaotic conversion oscillations in the range of ∼80–90%, most probably, being a result of the same oscillations between CSTR/plug-flow modes with influence of external mass-transfer limitations.

Certain attention was also paid to hypothesis, concerning possible presence of homogeneous gas-phase reaction, where highly reactive radicals are produced at catalysts surface. This hypothesis was privately discussed as a possible explanation of "light-off" behavior of the catalyst and it was to decided to clarify this question experimentally. It was proposed, that quartz support, situated under the catalyst, should be an excellent radical trap, therefore in case of radical mechanism the observed conversion in upflow and downflow directions of gas feeding (or, in other words, in different gas flow sequence: quartz/catalyst/free volume and vice versa) should be different.

Actually, performed experiments have not revealed such difference, therefore, radical hypothesis may be rejected and the reaction mechanism may be studied from conventional positions of heterogeneous catalysis.

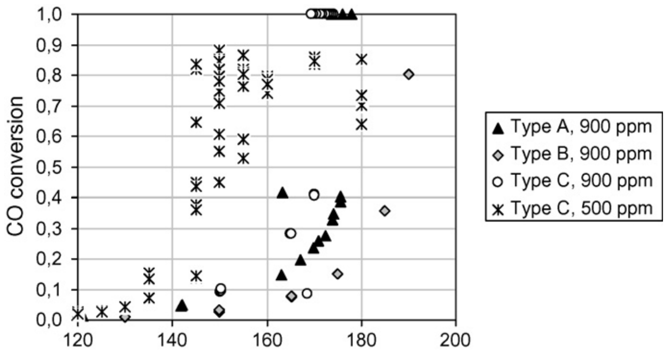

Fig. 4. Experimental data on CO conversion vs. temperature in different types of reactor arrangement. Residence time—0.21 s.

3. Reaction kinetics

The kinetic description of CO oxidation reaction at noble metal catalysts may be based on widely acknowledged mechanism, including following reaction steps:

$$CO + [O] \Rightarrow CO_2 + [\,] \tag{1}$$

$$[] + \tfrac{1}{2}O_2 \Rightarrow [O] \tag{2}$$

$$CO + [\,] \Leftrightarrow [CO] \tag{3}$$

CO oxidation rate in excess of oxygen in that case may be described by simplified kinetic expression:

$$w = \frac{k_1 C_{CO}}{1 + k_2 C_{CO}^2} \tag{4}$$

Determination of model parameters was based on experiments in type A reactor, due to more reliable attribution of reactor operation mode (CSTR) in comparison with other reactor types. Taking into account that experiments were performed at "glass-wool" state of the catalyst this kinetics may be considered as intrinsic one, not influenced by mass transfer limitations.

For CSTR Eq. (4) may be reformulated into:

$$\frac{C_{CO}^{in} - C_{CO}^{out}}{\tau} = \frac{k_1 C_{CO}^{out}}{1 + k_2 C_{CO,out}^2} \tag{5}$$

Presence of second order C_{CO} term in inhibition part of the equation leads to existence of three steady-state solutions. While one of them is known to be unstable, other two may be observed in experiments as high-conversion and low-conversion operation modes.

It is seen (Fig. 5) that the proposed model provides quite good agreement between calculated and experimental results for the catalyst "light-off" effect in CSTR mode for higher CO inlet concentration (900 ppmv). Calculations also showed that predicted plug-flow data are in good agreement with experiments in type B reactor. It is seen that experimental data for type C reactor belongs to both CSTR multiplicity area and plug flow curve, therefore, transitions between CSTR and plug flow modes are possible in case of thin-bed reactor.

The model also provides good description of CO conversion hysteresis phenomena under variation of residence time (Fig. 6) and many other experimental results obtained.

At the same time the model failed to describe experiments in type C reactor at lower concentration of CO (500 ppmv). Evidently, satisfactory agreement in this case may be achieved only on the basis of account of external mass transfer limitations in combination with account of axial diffusion mass transfer in a view of aforementioned possible transitions between CSTR and

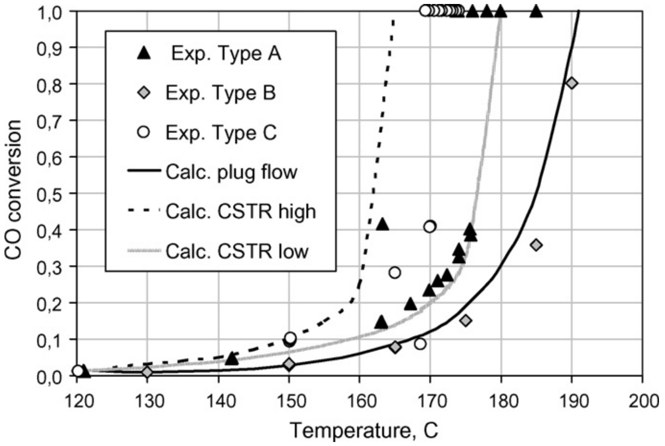

Fig. 5. Experimental and calculated values of CO conversion (for high/low conversion modes) in type A and B reactors. CO inlet concentration—900 ppmv, residence time—0.21 s. Points—experimental data, lines—calculated values.

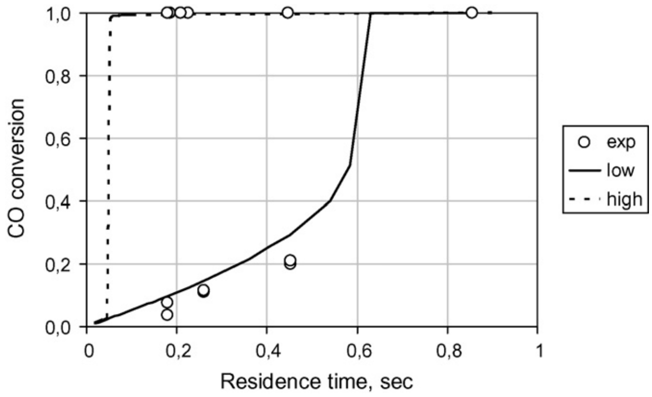

Fig. 6. Hysteresis of CO conversion under variation of residence time in type B reactor. CO concentration—500 ppmv, temperature—150 °C. Points—experimental data, lines—calculated values.

plug flow reactor operation modes, being a subject for separate future research.

4. Simulation of diffusion limitations inside the catalyst thread

The important question of prediction of fiber-glass catalysts behavior is influence of heat and mass transfer limitations inside the knitted thread of the catalyst.

It seems impossible to measure these effects experimentally, so this problem was studied by means of numerical simulation, using aforementioned kinetic model.

Earlier it was shown that important distinction of fibrous catalyst from conventional granular ones is possibility of existence of the convective flow inside the thread besides the usual conductive diffusion [2]. Nevertheless, under studied experimental conditions influence of such flows may be neglected because they may play significant role only at high gas linear velocities, as it was demonstrated in [6].

In our model formulation we proposed the single catalyst thread with internal diffusion of reagents and internal heat conductive transfer. The thread length exceeds significantly its diameter so it was possible to use the one-dimensional model of an endless cylinder [7] (see Fig. 7):

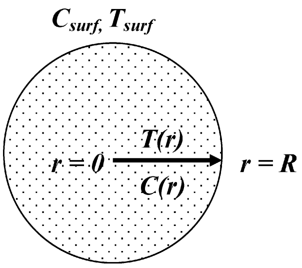

Fig. 7. Geometrical scheme for thread model (axial sequence of the thread).

$$D_{\mathrm{eff}}\left(\frac{\partial^2 C(r)}{\partial r^2}+\frac{1}{r}\frac{\partial C(r)}{\partial r}\right)=w(C(r),T(r)) \tag{6}$$

$$\lambda_{\mathrm{eff}}\left(\frac{\partial^2 T(r)}{\partial r^2}+\frac{1}{r}\frac{\partial T(r)}{\partial r}\right)+Qw(C(r),T(r))=0 \tag{7}$$

with boundary conditions:

$$\begin{aligned} &r=0 \Rightarrow \partial C(r)/\partial r=0; \quad \partial T(r)/\partial r=0,\\ &r=R \Rightarrow C(r)=C_{\mathrm{surf}}; \quad T(r)=T_{\mathrm{surf}} \end{aligned} \tag{8}$$

Kinetic expression $w(C, T)$ obtained above (4) was used. Value of efficient heat conductivity was estimated from the value of heat conductivity coefficient of reaction media balance gas, using the equation [7]:

$$\lambda_{\mathrm{eff}} \approx 10\lambda_{\mathrm{g}} \tag{9}$$

The channels between micro-fibers in the thread are relatively wide (typically–few microns), therefore, Knudsen type diffusion should not be taken into account and efficient CO diffusivity inside the thread may be with acceptable accuracy described by molecular diffusion coefficient with account of thread porosity:

$$D_{\mathrm{eff}}=\varepsilon D_{\mathrm{mol}} \tag{10}$$

Observed reaction rate was obtained by integration of local rate values along the thread radius after numerical solving the system (6)–(10) with determination of $C(r)$ and $T(r)$ functions:

$$W=\int_{r=0}^{r=R} w(C(r),T(r))r\,\mathrm{d}r \tag{11}$$

The results of simulation are given in Figs. 8–10. In general it was found that diffusion limitations may be significant even at low CO concentrations and moderate temperatures, leading to existence of two reaction modes with "high" and "low" reaction rates and temperature nonuniformity inside the thread.

In "low" conversion mode the thread is practically uniform and influence of diffusion limitations is negligible (Fig. 8). To the contrary, "high" conversion mode is characterized by the strong concentration nonuniformity, when the major part of conversion occurs in the thin intermediate zone between thread surface and thread axis (Fig. 9). Integral reaction rate in case of "high" conversion mode is higher than reaction rate at thread surface conditions and formal observed effectiveness factor may reach the values as high as 7–8.

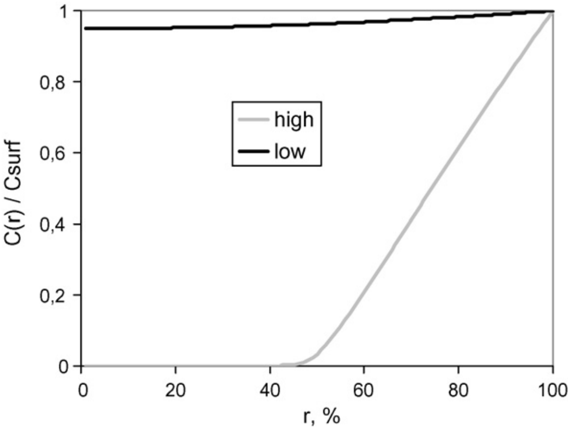

Fig. 8. Calculated relative local CO concentrations (related to concentration at the surface) in high/low conversion modes vs. catalyst thread radius. 0%—Thread axis, 100%—thread surface. *Thread surface conditions*: temperature 150 °C, CO concentration 500 ppmv, thread diameter 3 mm, $\varepsilon = 0.8$, balance media helium.

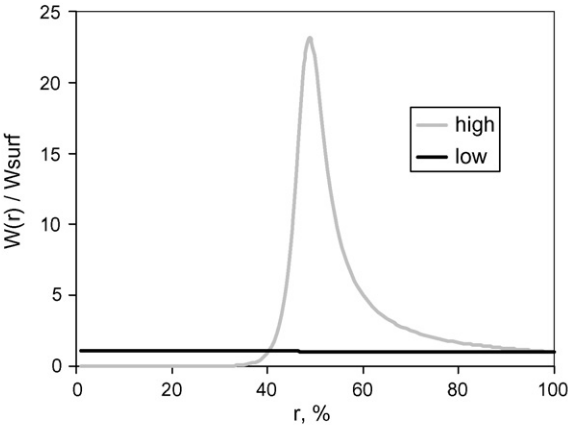

Fig. 9. Calculated relative local reaction rates (observed reaction rate in relation to rate at surface conditions) in high/low conversion modes vs. catalyst thread radius. *Conditions*—see Fig. 7.

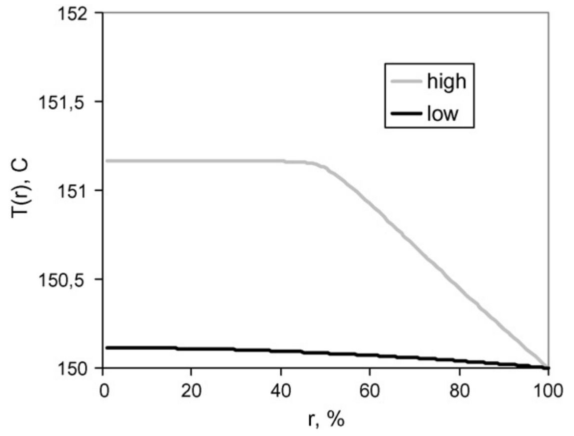

Fig. 10. Calculated catalyst temperature in high/low conversion modes vs. catalyst thread radius. *Conditions*—see Fig. 7.

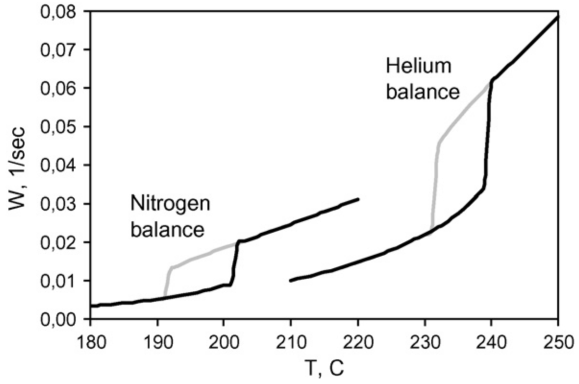

Fig. 11. "Light-off" reaction rate multiplicity regions for nitrogen-based and helium-based reaction media. Black/grey lines—low/high CO conversion regime, respectively. *Conditions*: CO concentration at thread surface—500 ppmv, thread diameter—3 mm, $\varepsilon = 0.8$.

The substantial temperature gradient (Fig. 10) is also observed. Though the value of temperature nonuniformity seem to be not high, the reaction "light-off" in definite temperature area (according to experimental data) may be caused by temperature changing by <1 °C, so this factor may impose significant influence on reaction performance.

The values of nonuniformities inside the thread depend upon many reaction conditions–thread diameter and porosity, CO surface concentration, surface temperature, etc. Notably, the simulation results may vary very much in simulations cases when balance gas was changed from helium to nitrogen (due to quite different values of effective diffusion and heat conductivity coefficients for these gases), as seen at Fig. 11. It means that investigations of practically important reactions (e.g. purification of gas exhausts, assuming oxygen and nitrogen as balance gases), using helium as balance gas (which is often applied for simplification of chromatographic analysis in lab experiments), may generally lead to erroneous results.

5. Summary

It may be summarized that reaction phenomena in fabric and threads of woven glass-fiber catalysts is rather complicated by transfer limitations, which may impose especially valuable influence on reactions with strongly non-linear kinetics, such as CO oxidation by oxygen at noble-metal based catalysts. Such limitations are related to extra-thread and intra-thread mass transfer. Additionally, in thin beds, consisting of one or few layers of woven catalyst, the significant role may be played by experimentally confirmed transient oscillations between CSTR and plug flow reactor operation modes, therefore, the axial heat and mass dispersion in the mathematical model for adequate simulation of such beds should not be neglected.

Mathematical modelling of phenomena inside the catalyst thread showed possibility of existence of steady-state multiplicity as a self-sufficient result of intra-thread transfer limitations. In general, observed reaction rates at the catalyst thread and location of multiplicity region may depend upon many factors (thread diameter and porosity, surface CO concentration and temperature and even choice of reaction media balance gas).

In general the experiments for research of catalyst performance and kinetic studies is recommended to perform using the catalyst in a form of separated fibers (“glass-wool”) to minimize transfer limitations and to get rid of mentioned complications. Recycle reactor (type A) application is worthy due to possibility of its attribution to CSTR type. Direct-flow reactor (type B) may be used as well as attributable to plug-flow type, though this attribution in this case is less reliable. The further transfer of obtained kinetic information in the scale up procedure for reactor development is possible on the basis of detailed mathematical modelling only. Such modelling should account for all levels of transfer limitations (extra/intra-thread and axial dispersion) and their conjugation. It should be noted, that very important questions of extra-thread transfer limitations (connected with geometry of glass-fiber catalyst fabrics and its issues of its optimization) was not discussed in current study and appear to be the subject of separate future study.

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