



Short communication

On the intra-fiber mass transfer limitations in glass-fiber catalysts

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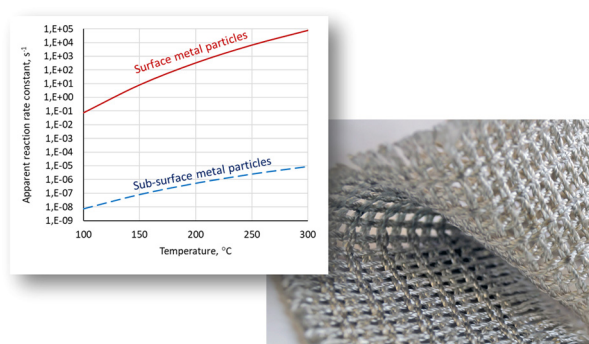
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HIGHLIGHTS

- Diffusion of reactants in glass bulk of glass-fiber catalysts considered.
- Surface and sub-surface location of the active component is compared.
- Surface location provide by 7–10 orders of magnitude higher apparent reaction rate.
- Sub-surface particles, even if exist, do not define the GFC catalytic properties.

GRAPHICAL ABSTRACT



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ABSTRACT

The study is dedicated to catalysts on the base glass microfibrinous supports. It discusses the issues of the diffusion of reactants in the bulk of glass fibers, using the model reaction of toluene deep oxidation in air at Pt-containing glass-fiber catalyst (GFC). The catalysts with location of Pt particles either at the external fiber surface or in the hypothetical sub-surface layers in the glass bulk are compared. The intra-fiber diffusion of toluene is considered from positions of diffusion in liquid, interpreting glass as super-cooled liquid with high viscosity. The calculations show that at moderate temperatures the diffusion coefficient and corresponding efficiency factor are extremely low due to very high viscosity of high-silica glasses. The apparent reaction rate at sub-surface Pt particles appears to be dramatically lower (by 7–10 orders of magnitude) than that for the surface Pt. It is concluded that even if the sub-surface metal particles really exist, their contribution to the overall performance of GFC is negligible. This result disproves the notion stating that properties of some class of GFCs are defined by sub-surface particles of active component.

1. Introduction

The glass-fiber catalysts (GFC) has received a lot of scientific interest during last two decades. Such catalysts use glass microfibers as support for various active components (Pt, Pd, transient metals oxides etc.). The microfibers are usually produced from non-porous high-silica glass and have a typical diameter of few microns. In the real GFC these

fibers are assembled into threads, which, in turn, are arranged into textiles of various structure.

GFCs demonstrate excellent catalytic performance in different catalytic reactions: oxidation of CO and organic compounds [1–5], oxidation of SO₂ [1,6] and H₂S [7], oxidation of chlorinated hydrocarbons [8], selective hydrogenation of acetylene [1,9,10] and others. This advantageous performance relates to both the high efficiency of

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Nomenclature

D	toluene diffusion coefficient inside the catalyst layer (m^2/s)
E	activation energy (kJ/mole)
h	thickness of external layer with metal particles (m)
k_0^m	kinetic pre-exponent ($\text{st.m}^3/(\text{g}_{\text{Pt}} \cdot \text{s})$)
k_B	Boltzmann constant (J/K)
k_v	kinetic rate constant, related to unit volume of sub-surface catalyst layer (1/s)

L	fiber length (m)
R	fiber radius (m)
r	toluene molecule radius (m)
R_g	universal gas constant (kJ/(mole * K))
T	temperature (K)
x_{Pt}	platinum content in the catalyst ($\text{g}_{\text{Pt}}/\text{kg}_{\text{cat}}$)
η	efficiency factor
μ	glass viscosity ($\text{Pa} \cdot \text{s}$)
φ	Thiele modulus
ρ_{GFC}	glass density ($\text{kg}_{\text{cat}}/\text{m}^3$)

external mass transfer in structured GFC packing [11,12] and the beneficial structure of active component. The external and intra-thread diffusion limitations in GFCs were studied earlier [11–13], but the intra-fiber diffusion was never considered quantitatively before.

In some earlier works, the high activity and operation stability observed for Pt-based GFC in reactions of deep oxidation of organic compounds were attributed to highly-dispersed platinum particles located under the glass fiber surface, in the glass bulk, at the depth up to 10–20 nm [1,2]. The similar sub-surface palladium particles were proposed as highly selective catalyst for hydrogenation of acetylene [1,9,10]. As soon as the glass support is considered as non-porous matter, it is believed that transport of reactants from fiber surface to sub-surface metal particles occurs via diffusion in the glass bulk like in liquid. This hypothesis is based on the interpretation of a glass as a super-cooled liquid with high viscosity.

This theory is under active discussion during last two decades. The evidences of existence of such sub-surface particles are indirect and not completely convincing. Moreover, even if such particles exist, it is not obvious that they are present in sufficient amount to provide the observed catalyst activity. Besides, in all synthesized GFCs at least the part of catalytically active metal is present at the external fiber surface, so it is impossible to distinguish the contribution of surface and sub-surface particles into overall catalyst performance. Therefore, any discussions on the catalytic properties of sub-surface species are not based on direct experimental data.

Putting aside the discussion on existence of sub-surface metal particles, we would like to pay special attention to transport of reactants in the glass bulk. If the sub-surface active species exist and if their amount is high enough, the rather high observed apparent reaction rates should be supported by sufficient mass transport of reactants from fiber surface to these particles and backward diffusion of reaction products. The given study was dedicated to theoretical evaluation of intra-fiber mass transfer limitations influence on apparent reaction rates at GFC with hypothetical sub-surface location of active component.

2. Fiber model

The GFC fiber may be represented as the long straight cylinder with the length L and radius R (Fig. 1a). Let us consider two geometrically different ways of supporting the active component: the active component is supported at the external surface of the fiber (Fig. 1b) or inside the fiber bulk layer with the thickness h (Fig. 1c).

For simplicity, let us assume that in the last case the active component is distributed uniformly across the volume of this layer and that it is completely absent from the external surface. For the correct comparison the unit amount of the active component was taken equal in both cases. The external surface of the fiber was considered as completely accessible for the reactants equally from all sides, absence of any external mass transport limitations was postulated.

The reaction of toluene deep oxidation in air was selected as the model reaction. We used the kinetic data for this reaction, related to commercial Pt-containing GFC IC-12-S111 with platinum content of 0.07% mass [12]. According to these data, the rate of toluene oxidation

in excess of oxygen may be described by the equation of the first-order type in respect to toluene concentration. The rate constant related to the unit fiber volume may be calculated as follows:

$$k = k_0^m \exp\left(\frac{-E}{R_g T}\right) \rho_{\text{GFC}} x_{\text{Pt}} \quad (1)$$

The mentioned catalyst was prepared using thermally pretreated non-leached glass fabric [4], having no internal voids for formation of active sub-surface structures. In this catalyst the sub-surface Pt location was completely excluded, therefore, the mentioned rate constant k corresponds to the GFC with completely surface location of Pt (Fig. 1b), characterized with absence of internal diffusion limitations.

In case of sub-surface Pt location (Fig. 1c) it is necessary to use the apparent rate constant:

$$k^* = \eta k \quad (2)$$

where η – efficiency factor, characterizing the influence of internal mass transfer limitations inside the catalytically active layer on the apparent reaction rate. Assuming $R \ll L$ and $h \ll R$, we may neglect the round shape of the catalytic layer, therefore, the efficiency factor may be calculated using the known equation for the flat one-dimensional system [14]:

$$\eta = \frac{ct h \varphi}{\varphi} \quad (3)$$

where φ – Thiele modulus, calculated as follows [14]:

$$\varphi = h \sqrt{\frac{k_v}{D}} \quad (4)$$

Rate constant k_v reflects the unit volumetric activity of the sub-surface layer and it is connected with constant k from equation (1), which is related to the whole fiber volume, by the ratio between the volume of fiber ($\pi R^2 L$) and volume of sub-surface catalytic layer ($2\pi R L h$):

$$k_v = \frac{k \pi R^2 L}{2\pi R L h} = \frac{k R}{2h} \quad (5)$$

Therefore, the equation (4) may be rearranged into:

$$\varphi = h \sqrt{\frac{k R}{2D h}} = \sqrt{\frac{k R h}{2D}} \quad (6)$$

Notably, surface location of Pt corresponds to $h = 0$, resulting in

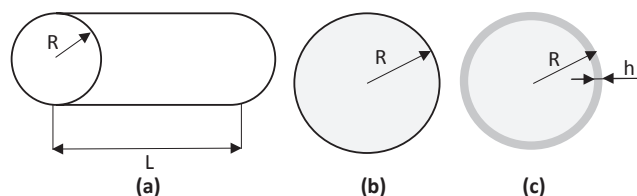


Fig. 1. The geometrical scheme of the catalyst fiber: a) – general view, b) catalyst with all active component located at the external surface of the glass fiber, c) catalyst with all active component located uniformly in the sub-surface layer in the external part of the glass fiber bulk volume.

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