Mathematical Model of the Carbon Monoxide Conversion in Porous Catalyst

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This article discusses the mathematical model of heat-build-up and component change in the multi-component gaseous mixture. The components take part in chemical reaction on a catalyst's solid surface. The mathematical model describes pre-oxidation reaction of carbon monoxide to carbon dioxide. Practical situation, accounted by the studied model is that CO afterburning to CO_2 takes place in automobile engine's exhaust gases for atmospheric condition improvement.

1. Introduction

The pre–oxidation reaction of carbon monoxide to carbon dioxide, with molecular oxygen, represents a simple but important reaction. This particular reaction has been researched for many years. It relates to oxidation of metals in platinum group, see Elokhin et al. (2010). This reaction shows the entire set of phenomena inherent in other more complex reactions, despite its simple kinetic mechanism. Such phenomena include chemical non-ideal, non-isothermal, critical behaviour, and diffusion, e.g. Tuttlies (2004), Bykov et al. (2005) and Deur et al. (2008).

This reaction is important for ecology. It takes place during deactivation of industrial wastes and exhaust automobile's gases, see, e.g. Alkemade et al. (2006) and Dvorak et al. (2010). Oxidation of carbon monoxide takes place in several stages. These stages are realised in the form of both knocking and non-knocking mechanisms (Ili–Ridil's and Lengmoore-Hanshelwood's mechanisms) as described by Ivanov et al. (1981).

In this work, a three-level descriptive scheme of catalytic conversion has been used. Two basic possibilities of such conversion are considered. The first one is the possibility under which oxygen, carbon, and carbon dioxide make up the whole gaseous mixture. The second one is when the above-mentioned gases are found in neutral gas medium. Their overall concentration is lower than that of the neutral medium. The first case is similar to processes in the field of chemical technology. The second corresponds to deactivation of motor vehicle's exhaust gases. The first level of the model apply to catalyst surface. It uses standard assumption on the presence of double transient scale of catalytic reaction (fast and slow). In relation to fast scale the transient equilibrium is achieved. Chemical kinetics equation is considered in steady state approximation of intermediary products, which are surface combinations with metals on the catalytic surface. Concentration of gaseous mixture components, subjected to conversion, plays

role in external adiabatically changing parameters in the equation of surface-catalytic kinetics, as described by Faber (2001) and Nayfen (1973).

At the second level, it's considered that moving gaseous mixture occupies some volume, which can be divided into the core and boundary layer. On this descriptive level hydrodynamics, heat and mass transfer in the boundary layer are analysed. Five interacting layers are considered. They are hydrodynamic, thermal and three diffusion layers, corresponding to the number of gaseous mixtures' components. For the cases under which components dissolved in inert gas, it's not necessary to consider diffusion boundary layer. The description is reduced to solution of thermal and hydrodynamic problems. Thermal problem can not be neglected, because of the considerable heat of reaction. It was discussed by Tsybenova (2008). The description includes interaction of all five boundary layers for such cases. Temperature drift (in the first case) and temperature and concentration drift (in the second case) of the mixture characteristics influence the results of surface catalytic reaction in both cases. These mixture characteristics include: viscosity, heat capacity and thermal conductivity. For the second description level, first level (surface catalytic reaction) brings boundary conditions for components' temperature and their respective concentrations in the gaseous mixture to the interior boundary of the boundary layers. Such approach may have, by justification, its condition. These catalytic processes takes place on the surface and that is influence on the mixtures' volume does not distribute further then the length of free run of the components' molecules.

During description of boundary layers' structure simple procedure is used according to Shvetz-Targ method, as described by Loytsyanskiy (1962). Its idea is that in the boundary layer, dependence of axial coordinates (relative to the layer) is eliminated in self-simulating (auto-modelled) variables and the remaining transverse variables are realized by averaging. Justification of the use of averaging operation and not iteration procedure, considered in Shvets-Targ method, is the circumstance that the computation results of the boundary layer's thickness are less apprehensible to the choice of initial approximation. The iteration procedure is itself cumbersome in the first two steps.

On the third description level, a model of moving gaseous mixture is considered with variable viscosity, heat capacity and thermal conductivity in the interior space created by the catalyst surface. The mixture is considered as a solid substance with spatially divided sources and outflow of both thermal and mass transfer nature. The concentrations of the components' mixture on the outer boundary are corresponding to their boundary layers. It delivers boundary condition for intermediate scale flow problem of gaseous mixture subjected to conversion. At this level of description, the flow of mixture occurs with hydraulic flow resistance, the values of which are determined by the catalytic surface on the intermediate scale.

2. Mathematical model

Mathematical model includes stability equations for intermediate adsorbed substances' concentration at the catalytic surface of carbon monoxide and carbon dioxide, equation for laminar hydrodynamics, heat transfer and mass transfer close to catalytic surface.

This model was chosen with such contemplation that the interior surface, through which gaseous mixture moves, should be formed by different parts made up of unconsolidated body. It's assumed that the interior surface consists of two-scaled elements, connected to each other. Hydraulic resistance for such a surface may be determined uniformly according to inertial effects of the moving gaseous mixture, intertwined with compression and expansion flow elements. Overall, interior surface is considered regular.

The description of thermal effects on the third level consists in plotting coefficient of thermal conductivity for two-phase substance. One of the phases is solid in the form of metallic framework. Upon it a layer of catalyst has been laid. The other phase is gaseous, in the form of gaseous mixture. During construction, combined cell method for mutually penetrating continuums is used, while the calculation itself goes according to Rele's method.

The classical Stephan-Maxwell equation is used in arrangement of expressions for concentration of streams in multi-components' mass transfer problem, as described by Kondepudi and Prigigine (1999). Coefficient of steam diffusion, which is part of the equation, depends on temperature in accordance to Sazerland's law, as was discussed by Missenard (1965). In order to draw correlation for mixtures' viscosity and thermal conductivity from temperature and concentration, the Mionar model was used. This model was chosen due to its simplicity and such feature that in this model, mutual influence of the gaseous mixtures' components with each other is accounted through changes in molecule's free path.

In this case, partial pressures for both carbon monoxide and dioxide are small. Equilibrium equations, written for intermediate products' chemical kinetics at the catalyst surface has such a constants of reaction rates, that it's possible to obtain solution for relative concentration in an explicit way. Laminar hydrodynamic equation interfaced with both heat and mass transfer may be solved, and velocity profile, temperature and gaseous mixture's concentration are derived as a function of the respective thickness of boundary layer. As a result, the following simultaneous equations are derived for conversion process description of gaseous mixture with molecular oxygen, carbon monoxide and dioxide in the presence of neutral gas (nitrogen) within the temperature range from 400 K to 800 K:

$$\frac{1}{3} \cdot \frac{\rho^* \cdot T^*}{T^\infty + \left(T_0 - T^\infty\right)\left(1 - \frac{\delta_w}{\delta_T}\right)} \cdot \left\{\frac{U^\infty}{\delta_w} \cdot \frac{\partial U^\infty}{\partial x} \cdot \left[1 - \frac{\left(T_0 - T^\infty\right) \cdot \left(1 - \frac{\delta_w}{\delta_T}\right) \cdot \frac{\delta_w}{\delta_T}}{T^\infty + \left(T_0 - T^\infty\right)\left(1 - \frac{\delta_w}{\delta_T}\right)^2}\right]\right\} =$$

$$= -\frac{2\mu\left(T_0\right)}{\delta_w^2} + \rho^* \cdot \frac{\partial U^\infty}{\partial x} \cdot \frac{T^*}{T^\infty + \left(T_0 - T^\infty\right)\left(1 - \frac{\delta_w}{\delta_T}\right)^2}$$

(1)

$$\frac{1}{3} \cdot \frac{\rho^* \cdot T^*}{T^\infty} \cdot Cp \cdot \left\{ 2U^\infty \cdot \frac{\partial T^\infty}{\partial x} - \frac{T_0 - T^\infty}{\delta_T} \cdot \left(\delta_T \cdot \frac{\partial U^\infty}{\partial x} + U^\infty \cdot \frac{\partial \delta_T}{\partial x} \right) \right\} =$$

$$= \frac{-2 \cdot r \cdot \dot{C}(T_0)}{\delta_T} \tag{2}$$

$$\frac{2}{3} \cdot U^\infty \frac{\partial C^\infty}{\partial x} - \frac{1}{3} \cdot (C_0 - C^\infty) \cdot \frac{\partial U^\infty}{\partial x} - \frac{1}{3} \cdot U^\infty \frac{\partial \delta_C}{\partial x} \cdot \frac{C_0 - C^\infty}{\delta_C} = -2 \cdot \frac{\dot{C}(T_0)}{\delta_C} \tag{3}$$

Equations (1) – (3) are connected simultaneous equations for thicknesses of hydrodynamic boundary layer – δ_w; temperature boundary layer – δ_T, diffusion boundary layer – δ_C for carbon monoxide. Values δ_w, δ_T, δ_C depend on temperatures T_0 and T^∞, concentrations C_0 and C^∞ at the surface and exterior boundary of layer, respectively.

Following Equations (4) and (5) describe changes in temperature for gaseous mixture T^∞ and carbon dioxide concentration C^∞ in a porous catalyst substances' mixture.

$$U^\infty \frac{\partial C^\infty}{\partial x} = \frac{D(T^\infty)}{\delta_C^2} (C_0 - C^\infty) \tag{4}$$

$$\frac{\rho^* \cdot T^*}{T^\infty} Cp \cdot U^\infty \frac{\partial T^\infty}{\partial x} = \frac{\lambda(T^\infty)}{\delta_T^2} (T_0 - T^\infty) \tag{5}$$

Equations (6) and (7) connect between each other temperature and concentration at the catalytic surface and in the stream at gaseous mixture.

$$T_0 = T^\infty + \frac{r\dot{C}(T_0)}{2\lambda(T_0)} \delta_T \tag{6}$$

$$C_0 = C^\infty + \frac{\dot{C}(T_0)}{2D(T_0)} \delta_C \tag{7}$$

Dependence of gaseous mixture transport coefficients from temperature T_0 and T^∞:

$$\lambda(T_0) = \lambda^* \cdot \frac{T^* + C_\lambda}{T_0 + C_\lambda} \cdot \left(\frac{T_0}{T^*} \right)^{\frac{3}{2}} \tag{8}$$

$$\lambda(T^{\infty}) = \lambda * \cdot \frac{T*+C_{\lambda}}{T^{\infty}+C_{\lambda}} \cdot \left(\frac{T^{\infty}}{T*}\right)^{\frac{3}{2}} \tag{9}$$

$$\mu(T_0) = \mu * \cdot \frac{T*+C_{\mu}}{T^{\infty}+C_{\lambda}} \cdot \left(\frac{T^{\infty}}{T*}\right)^{\frac{3}{2}} \tag{10}$$

$$\mu(T^{\infty}) = \mu * \cdot \frac{T*+C_{\mu}}{T^{\infty}+C_{\mu}} \cdot \left(\frac{T^{\infty}}{T*}\right)^{\frac{3}{2}} \tag{11}$$

$$D(T_0) = D(T*) \cdot \left(\frac{T^0}{T*}\right)^{1,85} \tag{12}$$

$$D(T^{\infty}) = D(T*) \cdot \left(\frac{T^{\infty}}{T*}\right)^{1,85} \tag{13}$$

The rate of carbon dioxide production ,as a function of molecular oxygen concentration on catalyst surface x_s and concentrations of oxygen' a_H and carbon monoxide b_H in gaseous mixture at the entrance of catalytic volume can be described as follows:

$$\dot{C}(T_0) = \frac{k_2^+ \cdot k_3 \cdot (b_H - C_0) \cdot x_s \cdot (1-x_s)}{k_2^+ \cdot (b_H - C_0) + k_2^- + k_3 x_s} + k_4 \cdot (b_H - C_0) \cdot x_s \tag{14}$$

$$x_s = \frac{\sqrt{m} \cdot e^{\frac{A}{T_0}} \cdot \sqrt{2 \cdot a_H - C_0}}{1 + \sqrt{m} \cdot e^{\frac{A}{T_0}} \cdot \sqrt{2 \cdot a_H - C_0}} \cdot \frac{2 \cdot a_H - C_0}{(2 \cdot a_H - C_0) + (b_H - C_0)} + $$
$$+ \frac{\sqrt{n} \cdot e^{\frac{B}{T_0}} \cdot \sqrt{\frac{(2 \cdot a_H - C_0)}{(b_H - C_0)^3}}}{1 + \sqrt{n} \cdot e^{\frac{B}{T_0}} \cdot \sqrt{\frac{(2 \cdot a_H - C_0)}{(b_H - C_0)^3}}} \cdot \frac{b_H - C_0}{(2 \cdot a_H - C_0) + (b_H - C_0)} \tag{15}$$

Equation (15) describes oxygen concentration on surface, that depends on the values of *m, n, A, B*. These values are derived from constants of reaction rate for carbon monoxide $k_1^{\pm}$, $k_2^{\pm}$, k_3, k_4 and activation energy of superficial reaction.

3. Conclusions

The description presented in this work has the following properties:

1. Chemical–kinetic effects determine boundary conditions and may include any kinetic-catalytic reaction differing from the analyzed in this work;

2. Localized laminar flow regime for gaseous mixture may be substituted by localized turbulent ones;

3. Models of gaseous mixture cumulative and transport properties are automatically suitable for any quantities of components;

4. Relationship between velocities of the streams' core at the external boundary of hydrodynamic boundary layer and mean volumetric flow velocity of gaseous mixture at the interior space of the catalytic substance is determined by pore's geometry.

References

Alkamade U. G. and Schumann B., 2006, Engines and exhaust after treatment systems for future automotive applications. Solid State Ionics, 177, 2291-2296.

Bykov V. I., Kiselev N. V. and Kiselev V. M., 2005, The influence of diffusion, size and geometry of the surface of a solid catalyst on the rate of catalytic reaction. Series of Physical and Mathematical Sciences, 9, 167-173.

Deur J. M., 2008, Simulation of Engine Exhaust Aftertreatment with CFD using detailed chemistry. Environmental Engineering Science, 25 (7), 1017-1036.

Dvorak R., 2010, Catalytic Filtration of Flue Gases Polluted by NOx. Chemical Engeneering Transactions, 21, 799-804.

Elokhin V.I., Matveev A.V., Kovalyov E.V. and Gorodetskii V.V., 2009, From single crystals to supported nanoparticles in oscillatory behavior of $CO+O_2$ reaction on platinum and palladium surfaces: Experiment and stochastic models. Chemical Engineering Journal, 154, 94–106.

Faber T. E., 2001, Hydrodynamics. Postmarket, Moscow, Russia, (in Russian).

Ivanov V. P., Elokhin V. I. and Yablonsky G. S., 1981, Kinetic model for the oxidation of CO on platinum group metals. Kinetics and Catalysis, 22 (4), 1040-1047.

Kondepudi D. and Prigigine J., 1999, Modern thermodynamics. From heat Engines to dissipative structures. J. Wiley and Sons, New York, USA.

Loytsyanskiy L. G., 1962, Laminar Boundary Layer. State Publishing House of Physico-Mathematical Literature, Moscow, Russia (in Russian).

Missenard A., 1965, Thermal Conductivity of solids, liquids and gases. Eyrolles, Paris, France (in French).

Nayfen Ali Hasan, 1973, Perturbation methods. Wiley and Sons, New York, USA.

Tsybenova S. B., 2008, Basic models of thermal kinetics. Physical and Chemical Kinetics in Gas Dynamics, 6, 44-66.

Tuttlies U., Schueisser V. and Eigenberger G., 2004, A mechanistic simulation model for NOx storage catalyst dynamics. Chemical Engineering Science, 59 (23), 4731-4738.