

## A Multi-Level Mathematical Model of the CO Catalytic Conversion Process

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This paper presents a three-level modelling approach to the catalytic carbon monoxide oxidation in a temperature range between 400 K – 800 K. The first level involves the description of the chemical kinetics for the exothermic reactions on the catalyst surface. The second level models the thermal and hydrodynamic processes in the boundary diffusion layer between the catalyst surface and the reactive stream. Finally, the third modelling level focuses on the representation of the hydrodynamic and thermal properties for the bulk multi-component gas flow at various gas velocity and temperature ranges. The dynamic behaviour of the reactive system has been studied through simulated runs.

### 1. Introduction

The oxidation reaction of CO to CO<sub>2</sub> with molecular oxygen represents an industrially important reaction system whose description involves multiple phenomena despite its simple kinetic mechanism (Bykov et al., 2005). The reaction takes place during deactivation of industrial waste as described by Arash E. (2012). The same reaction in automobile exhaust gas conversion unit was studied by Dvorak R. (2010). Oxidation of carbon monoxide takes place in several stages through either Ili–Ridil or Lengmoore–Hanshelwood mechanism. In this work, a multi-level mathematical model of catalytic conversion has been developed as initially suggested by Ved et al. (2011a). The model considers both the case where oxygen, carbon monoxide and carbon dioxide make up the gaseous mixture and the case where the reactive mixture is mixed with a neutral medium.

### 2. Mathematical model

The first level of description refers to a catalytic surface. The reaction proceeds by passing the gas mixture through a catalytic converter. Platinum catalytic active centers are located on the surface of a uniformly distributed metal carrier. Metal supports are made of thin wire-based high-temperature alloys. CO molecules collide with the surface of the support, but do not limit the diffusion of the reacting gas from the bulk to the catalyst surface. Figure 1 shows schematic of the reaction on the surface of catalyst

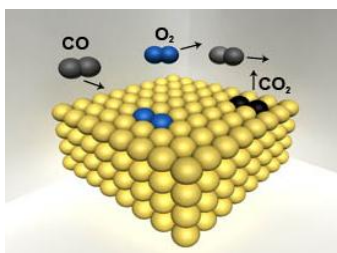
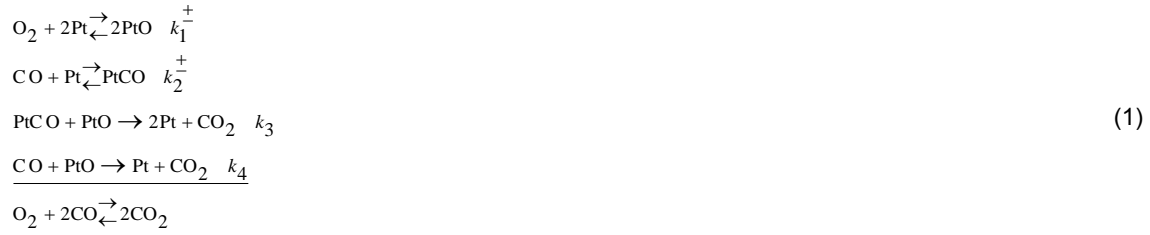


Figure 1. Schem of the reation on the surface of the catalyst

The general form of the oxidation mechanism is as follows:



Symbols  $k_1^\pm$ ,  $k_2^\pm$ ,  $k_3$ ,  $k_4$  denote the Arrhenius reaction rate constants. Below approximated model is presented. The full mathematical model of the first level was described in Ved et al. (2010a).

$$\frac{\partial c}{\partial t}(T_0) = \frac{k_2^+ \cdot k_3 \cdot (b_s - C_0) \cdot x_s \cdot (1 - x_s)}{k_2^+ \cdot (b_s - C_0) + k_2^- + k_3 x_s} + k_4 \cdot (b_s - C_0) \cdot x_s \tag{2}$$

$$x_s = \frac{\frac{\sqrt{me}}{1 + \sqrt{me}} \frac{A}{T_0} \sqrt{2a_s - C_0}}{\frac{\sqrt{me}}{1 + \sqrt{me}} \frac{A}{T_0} \sqrt{2a_s - C_0} + \frac{2a_s - C_0}{(2a_s - C_0) + (b_s - C_0)} + \frac{\sqrt{ne} \frac{B}{T_0} \sqrt{(2a_s - C_0)(b_s - C_0)^3}}{1 + \sqrt{ne} \frac{B}{T_0} \sqrt{(2a_s - C_0)(b_s - C_0)^3}}} \tag{3}$$

Symbols  $a_n$  and  $b_n$  denote the oxygen concentration and carbon monoxide surface concentration at the entrance to catalytic volume;  $C_0$  denotes values of  $\text{CO}_2$  concentrations on the solid catalytic surface;  $x_s$  denotes the concentration of molecular oxygen;  $T_0$  denotes the mixture temperature on the solid catalytic surface. Eq. (2) describes the rate of carbon dioxide production on the catalytic surface as a function of the surface concentration of molecular oxygen  $x_s$  and the concentrations of oxygen. Eq. (3) describes the concentration of surface oxygen that depends on the quantities  $m$ ,  $n$ ,  $A$ , and  $B$ . These quantities are derived from the reaction rate constants for the oxidation of carbon monoxide  $k_1^\pm$ ,  $k_2^\pm$ ,  $k_3$ ,  $k_4$  and the activation energies of surface reactions.

The second level of the mathematical model aims to describe the boundary layer phenomena. Specifically, the hydrodynamics, heat transfer, and mass transfer along the boundary layer and their interaction with the bulk flow of the reactive stream are considered. Hydrodynamic, heat and mass transfer mechanisms are fully coupled and therefore must be solved simultaneously. In particular, the thicknesses of the velocity, temperature and concentration boundary layers strongly affect the energy and material balances within the boundary layer. Surface catalytic reactions influence the temperature and concentration of all mixture components that subsequently alter the mixture thermodynamic characteristics such as viscosity, thermal conductivity, and heat capacity. In the case of dilute reactive mixtures only the thermal effects to the mixture characteristics are taken into account. The first level solution at the catalyst surface determines the boundary conditions for the temperature and concentrations in the diffusion layers. This approach can be justified by the fact that the reactions on the surface occur in such a way that their influence on the volume of the reaction mixture does not reach further than the free path length of the molecules of the components. The approximated model derived from the full order model presented by Ved et al. (2010b) is formulated as follows:

$$\frac{1}{3} \frac{\rho^* T^*}{T_1 + (T_0 - T_1) \left(1 - \frac{\delta_w}{\delta_T}\right)} \left\{ \frac{U_1}{\delta_w} \frac{\partial U_1}{\partial x} \left[ 1 - \frac{(T_0 - T_1) \left(1 - \frac{\delta_w}{\delta_T}\right) \frac{\delta_w}{\delta_T}}{T_1 + (T_0 - T_1) \left(1 - \frac{\delta_w}{\delta_T}\right)^2} \right] \right\} = -\frac{2\mu(T_0)}{\delta_w^2} + \rho^* \frac{\partial U_1}{\partial x} \frac{T^*}{T_1 + (T_0 - T_1) \left(1 - \frac{\delta_w}{\delta_T}\right)^2} \tag{4}$$

$$\frac{1}{3} \cdot \frac{\rho^* \cdot T^*}{T_1} \cdot C_p \cdot \left\{ 2U_1 \cdot \frac{\partial T_1}{\partial x} - \frac{T_0 - T_1}{\delta_T} \cdot \left( \delta_T \cdot \frac{\partial U_1}{\partial x} + U_1 \cdot \frac{\partial \delta_T}{\partial x} \right) \right\} = \frac{-2 \cdot r \cdot \frac{\partial c}{\partial t}(T_0)}{\delta_T} \tag{5}$$

$$\frac{2}{3} \cdot U_1 \frac{\partial C_1}{\partial x} - \frac{1}{3} \cdot (C_0 - C_1) \cdot \frac{\partial U_1}{\partial x} - \frac{1}{3} \cdot U_1 \frac{\partial \delta_C}{\partial x} \cdot \frac{C_0 - C_1}{\delta_C} = -2 \cdot \frac{\frac{\partial c}{\partial t}(T_0)}{\delta_C} \quad (6)$$

$$T_0 = T_1 + \frac{r \frac{\partial c}{\partial t}(T_0)}{2\lambda(T_0)} \delta_T \quad C_0 = C_1 + \frac{\frac{\partial c}{\partial t}(T_0)}{2D(T_0)} \delta_c \quad (7)$$

$$\lambda(T_0) = \lambda^* \cdot \frac{T^* + C_\lambda}{T_0 + C_\lambda} \cdot \left(\frac{T_0}{T^*}\right)^{\frac{3}{2}} \quad \mu(T_0) = \mu^* \cdot \frac{T^* + C_\mu}{T_1 + C_\mu} \cdot \left(\frac{T_0}{T^*}\right)^{\frac{3}{2}} \quad D(T_0) = D(T^*) \cdot \left(\frac{T_0}{T^*}\right)^{1,85} \quad (8)$$

$$\mu(T_1) = \mu^* \cdot \frac{T^* + C_\mu}{T_1 + C_\mu} \cdot \left(\frac{T_1}{T^*}\right)^{\frac{3}{2}} \quad \lambda(T_1) = \lambda^* \cdot \frac{T^* + C_\lambda}{T_1 + C_\lambda} \cdot \left(\frac{T_1}{T^*}\right)^{\frac{3}{2}} \quad D(T_1) = D(T^*) \cdot \left(\frac{T_1}{T^*}\right)^{1,85} \quad (9)$$

Symbols  $\lambda^*$ ,  $\mu^*$ ,  $\rho^*$ ,  $D^*$ ,  $T^*$  denote the thermal conductivity, viscosity, density, diffusion coefficient and temperature of molecular nitrogen under normal conditions, respectively;  $C_\lambda$ ,  $C_\mu$ ,  $C_\rho$  denote Sutherland constants for thermal conductivity, viscosity, and density of the gas mixture, respectively;  $r$  denotes the coefficient of the thermal effect of the reaction;  $\delta_w$ ,  $\delta_T$ ,  $\delta_c$  denote the thicknesses of the hydrodynamic, thermal, and diffusion boundary layers, respectively.  $T_0$  and  $T_1$  stand for the mixture temperature on the solid catalytic surface and in the bulk flow,  $C_0$  and  $C_1$  denote the values of CO<sub>2</sub> concentrations on the solid catalytic surface and in the bulk flow;  $U_1$  denotes the velocity of a mixture in the bulk flow. Eq(4) – Eq(6) are a set of coupled equations for the thicknesses of the hydrodynamic boundary layer  $\delta_w$ , the thermal boundary layer  $\delta_T$ , and the diffusion boundary layer  $\delta_c$  for CO<sub>2</sub>, respectively. The quantities  $\delta_w$ ,  $\delta_T$ , and  $\delta_c$  depend on the temperatures  $T_0$  and  $T_1$  and the concentrations  $C_0$  and  $C_1$  on the surface and outside the corresponding boundary layers. Eq(7) relates the values of temperatures and concentrations on the surface of a catalyst and in a gas flow in the catalyst pores. Eq(8) – Eq(9) establish the dependences of the transport coefficients of a gas mixture on the temperatures  $T_0$  and  $T_1$ .

The third level of the mathematical model describes the behavior of the bulk flow in the reactor. At the third level of description, the model of motion of a gas mixture with variable viscosity, heat capacity, and thermal conductivity in the internal space formed by the surface of a catalyst is considered. A mixture is assumed to be a continuous medium with spatially distributed sources and sinks for mass and energy. Temperature and mixture composition on the boundary layer – bulk flow interface is responsible for the interaction among the modeling levels. The bulk flow of a mixture faces hydraulic resistance whose value is affected by the structure of a catalytic surface. The description of the thermal effects on the third level depends on the thermal conductivity properties of the two-phase (gas-solid) medium. Solid-phase is a metal frame on which a layer of catalyst is deposited. In the construction method uses a combination of cells by the method of Reley. Stefan-Maxwell equations described by Taylor and Krishna (1993) are employed for the calculation of the concentration profiles. Diffusion coefficients, which are included in these equations, depend on the temperature according to Sutherland. To construct a function of temperature and concentration on the viscosity and thermal conductivity of the mixture Misnar's model was used. The full description of the model was discussed in Ved (2011b). The approximated model is presented below.

$$U_1 \frac{\partial C_1}{\partial x} = \frac{D(T_1)}{\delta_c^2} (C_0 - C_1) \quad (10)$$

$$\frac{\rho^* \cdot T^*}{T_1} C_p \cdot U_1 \frac{\partial T_1}{\partial x} = \frac{\lambda(T_1)}{\delta_T^2} (T_0 - T_1) \quad (11)$$

Symbols  $C_0$  and  $C_1$  denote the values of CO<sub>2</sub> concentrations on the solid catalytic surface and in the flow core;  $T_0$  and  $T_1$  values of the mixture temperature on the solid catalytic surface and in the flow core,  $\delta_T$ ,  $\delta_c$  denote the thicknesses of the thermal and diffusion boundary layers;  $\rho^*$  and  $T^*$  denote the density, and temperature of molecular nitrogen under normal conditions. Eq.(10) and Eq.(11) describe the variation of

the temperature of a gas mixture  $T_1$  and  $C_1$  the concentration of  $\text{CO}_2$  in the mixture in the internal space of a catalyst. In the third-level model is also included the model equations described second level.

Another level of mathematical model description of the fourth model relates to the previous levels of the model structure of the catalyst. This level refers to the scale of the reactor and describes hydrodynamic and thermal characteristics of the core concentration in the flow stream in the catalyst mixture. To describe this level should be set the boundary conditions for pressure, temperature rate of concentration at the input and the output of the catalyst. All of these levels represent an open system. The model presented in this study is intended for describing the hydrodynamic and heat and mass transfer behavior of a mixture of gases in the reaction of CO oxidation in the approximation of the laminar character of the boundary layers in the temperature range that does not exceed 1,000 K. The model admits an extension to a turbulent flow regime without changing its methodological principles. The description has the following properties: chemical kinetic effects determine boundary conditions and can include any kinetics of catalytic reactions that is different from one considered in this study and the locally laminar flow regime of a gas mixture can be replaced by a locally turbulent flow regime. The relationship between the velocity of a flow core on the external boundary of the hydrodynamic boundary layer,  $U_1$ , and the volume averaged velocity of a gas mixture in the internal space of a catalytic medium is determined by the pore geometry. The structure of the model is such that the equations of the first level of description are included as an individual unit; therefore, the equations of the second and third levels of mathematical model include individual terms generated by the first level of description. This means that the presented model can be extended to other catalytic reactions. An increase in the number of components of a gas mixture for other reactions changes the number of diffusion layers and equations at the second and third levels of mathematical model. Other ways of organization a catalytic surface require other models. However the model blocks used in the full model can be used in describing any construction of internal surface.

### 3. Results and discussion

The simulation results of the first-level model are shown in Figure 2 – Figure 4. Figure 2 - Figure 4 represented an oxidation reaction with in relation to  $\text{CO}_2$  adsorption of  $\text{O}_2$  and CO and  $\text{CO}_2$  formation. The simulation was performed under the conditions of temperature  $T = 500$  K, the partial pressure of the input parameters of CO and  $\text{O}_2$   $P(\text{CO}) = 2 \times 10^{-3}$ ,  $P(\text{O}_2) = 2.5 \times 10^{-2}$  respectively. The initial concentrations of CO and  $\text{O}_2$  are  $C(\text{CO}) = 80\%$ ,  $C(\text{O}_2) = 20\%$  Figure 2;  $C(\text{CO}) = 68\%$ ,  $C(\text{O}_2) = 32\%$  Figure 2;  $C(\text{CO}) = 67\%$ ,  $C(\text{O}_2) = 33\%$  Figure 3;

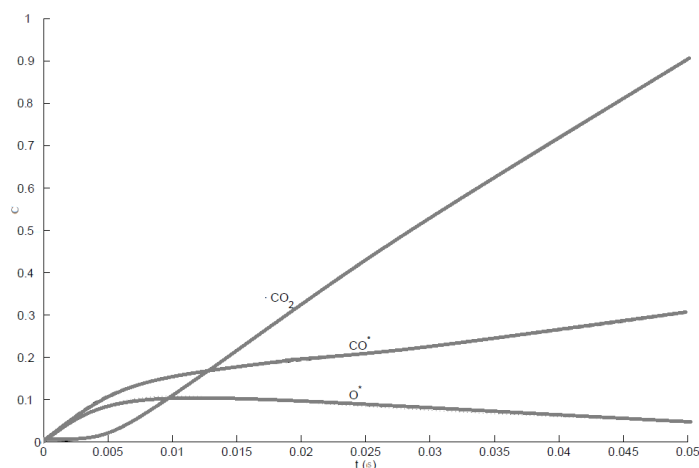


Figure 2. Scheme catalytic synthesis of carbon monoxide; the initial concentrations are  $C(\text{CO}) = 80\%$ ,  $C(\text{O}_2) = 20\%$

Symbols  $\text{CO}^*$ ,  $\text{O}^*$ ,  $\text{CO}_2$  denote the concentration of adsorbed CO, concentration of adsorbed  $\text{O}_2$  and concentration of  $\text{CO}_2$  respectively.

The initial stage of the reaction is characterized by a high degree of adsorption of CO. amount of adsorbed CO increases compared with adsorbed  $\text{O}_2$ . In the beginning of the reaction of adsorbed CO and  $\text{O}_2$  are practically identical. Rapid formation of the product leads to a decrease of  $\text{CO}_2$  adsorbed  $\text{O}_2$  which

is in deficit. As a result, the surface of the adsorbed CO is dialed in place of which the surface layer is formed by the product of CO<sub>2</sub> see Figure 2.

The significant dominance of the adsorbed oxygen is constantly disappears, the amount on the surface decreases to zero. At the same time begins to increase the amount of adsorbed CO. This is due to the fact that the first due to decomposition reaction of the oxygen molecules into atoms adsorbed oxygen concentration increases dramatically and gives the possibility to use almost all of the adsorbed molecules on the formation of a product with CO<sub>2</sub>. At the end of the reaction is still an excess of CO molecules are adsorbed and remain on the catalyst surface see Figure 3

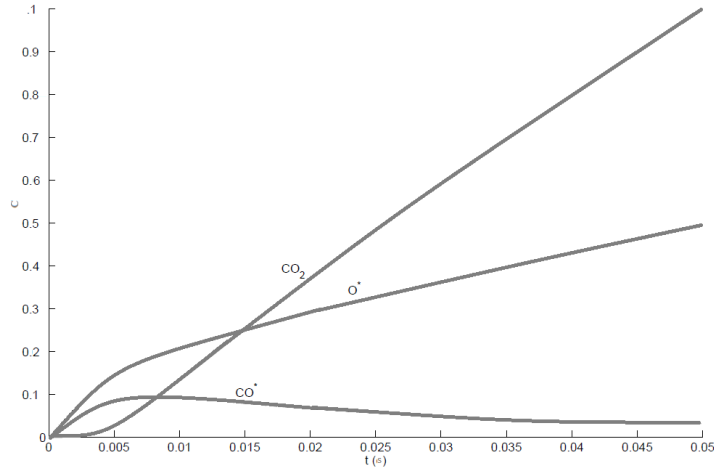


Figure 3. Scheme catalytic synthesis of carbon monoxide; the initial concentrations are  $C(\text{CO}) = 68 \%$ ,  $C(\text{O}_2) = 32 \%$

It can be seen Figure 4 that the product formed CO<sub>2</sub> reaches a maximum. In comparison with the previous cases Figure 2, Figure 3 is completely full of CO and O<sub>2</sub> are used to form CO<sub>2</sub>. The process of the reaction, accompanied by the constant formation of CO<sub>2</sub>. As a first reaction, and later the concentration of O<sub>2</sub> is much higher than the CO concentration.

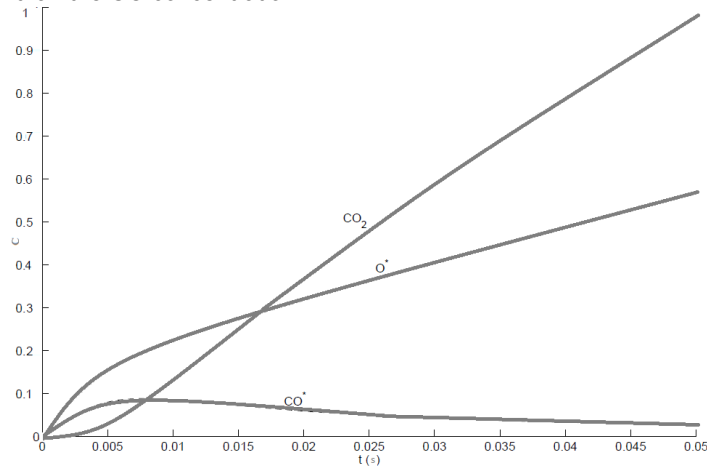


Figure 4. Scheme catalytic synthesis of carbon monoxide; the initial concentrations are  $C(\text{CO}) = 67 \%$ ,  $C(\text{O}_2) = 33 \%$

#### 4. Conclusions

A three level model for the catalytic oxidation of CO to CO<sub>2</sub> has been presented. The model describes surface, boundary layers, bulk flow and diffusion phenomena. The structural form of the model enables the easy extension to other catalytic reactive systems.

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