A Mathematical Model of the Catalytic Heat-Coupled Reactor of Steam Methanol Reforming

<u>Kirillov V.A.</u>, Shigarov A.B., Kuzin N.A., Kireenkov V.V. Boreskov Institute of Catalysis, Prosp. Akademika Lavrentieva, 5, 630090 Novosibirsk.

Mathematical model is developed to analyze the operation of a compact catalytic reactor. The reactor is based on the principle of heat coupling of endothermic steam reforming methanol and methanol exothermic catalytic combustion.

1. Introduction

In recent years, the progress in hydrogen energy has launched problem of development of compact catalytic reactors for generation of synthesis gas from different oxygencontaining hydrocarbon fuels (methanol, bio ethanol, dimethyl ether etc), which will be utilized in fuel cell power plants. Steam reforming provides the maximal hydrogen yield, but it requires heat supply to the endothermic reaction zone. One promising solution of the problem is heat coupling (in one reactor) of the endothermic reaction of steam-methanol reforming and catalytic afterburning of the hydrogen-containing anode gas unspent in the fuel-cell stack (S. Nagano et al., 2002; L. Pan and S. Wang, 2005; J. Lattner and M. Harold, 2005; W. Cao, 2006). In our case, the reactor is designed as a combination of 2 units, connected by heat transfer. The first unit consists of the channels for endothermic steam reforming of methanol (endothermic channels), where the following reactions take place: methanol steam reforming: $CH_4O + H_2O = CO_2 + CO_2 +$ 3H₂; shift-reaction: $CO + H_2O = CO_2 + H_2$; methanol decomposition: $CH_4O = CO + H_2O = CO_2 + H_2$; methanol decomposition: $CH_4O = CO_2 + H_2$; methan 2H₂. The second unit consists of the flat channels with catalytically active walls, where following exothermic reaction proceeds: methanol oxidation: the $CH_4O + 1.5O_2 = CO_2 + 2H_2O$. A reactor scheme is shown in Fig. 1.



The evolved heat is transferred to the neighboring endothermic channels due to heat conductivity. Such type reactors were discussed in the literature; a number of mathematical models describing stationary regimes have been suggested. Recently, these reactors have attracted considerable interest because of the development of high-temperature proton exchange membrane fuel cells (HT PEMFCs) exhibiting low sensitivity to CO concentration in synthesis gas (A. Reiche et al., 2006). The use of methanol for generation of hydrogen-containing gas using steam reforming at

 $H_2O/MEOH > 1.3$ permits one to obtain CO concentration about 1-1.5% in the reaction products, which is suitable for direct feeding of the above gas into a HT PEMFC stack. In this work we suggest a mathematical model for describing processes occurring in the reactor and present the experimental data on the steam methanol reforming and their comparison with the simulated results.

2. Mathematical model

A mathematical model of the processes occurring in the endothermic channels is twodimensional model. The heat-balance equations take into account both axial convective heat transfer by gas, radial conductive heat transfer along the reforming catalyst and heat exchange between gas and a catalyst. The material balance equations take into account the reaction of steam methanol reforming, shift reactions and methanol decomposition (which occur in the kinetic mode).

Equations of heat and material balance for endothermic channels $0 \le 1 \le 1$, $0 \le \ell \le 1$,

$$\begin{aligned} G_{en} \frac{\partial y_i}{\partial \ell} &= \left(v_i^{con} W_{con} + v_i^{dec} W_{dec} + v_i^{sh} W_{sh} \right) m_i, i = \{ H_2 O, CH_4 O, H_2, CO, CO_2 \} \\ c_p^{en} G_{en} \frac{\partial T_g^{en}}{\partial \ell} &= \alpha_{en} S \left(T_c - T_g^{en} \right), \\ \lambda_z \frac{\partial^2 T_c}{\partial z^2} + \Delta H_{con} W_{con} + \Delta H_{dec} W_{dec} + \Delta H_{sh} W_{sh} = \alpha_{en} S \left(T_c - T_g^{en} \right), \end{aligned}$$

A mathematical model of the processes occurring in the exothermal channels is a onedimensional model of plug-flow reactor. The material-balance equation takes into account the oxidation of methanol, whose apparent rate is determined by both kinetics and external mass transfer. The heat balance equations take into account both convective heat transfers by gas, heat exchange between gas and the oxidation catalyst (which is sintered with the metal wall) as well as the axial heat conductivity of the metal wall.

Equations of heat and material balance for exothermal channels $0 \le \ell \le L$,

$$c_{p}^{ex}g\frac{dT_{g}^{ex}}{d\ell} = \alpha_{ex}(T_{W} - T_{g}^{ex})$$

$$g\frac{dx_{j}}{d\ell} = v_{j}^{met}w_{CH_{4}O}^{ox}m_{j}, \qquad j = \{CH_{4}O, N_{2}, O_{2}, CO_{2}, H_{2}O_{3}\},$$

Boundary conditions: at $\ell = 0$, $0 \le z \le H$: $\frac{dT_w}{d\ell} = 0$, $y_i = y_{i0}$, $x_j = x_{j0}$, $T_g^{en} = T_{g0}^{en}$, $T_g^{ex} = T_{g0}^{ex}$. at $\ell = \mathbf{L}$: $\frac{dT_w}{d\ell} = 0$. at z = 0, $0 \le \ell \le \mathbf{L}$: $\frac{\partial T_c}{\partial z} = 0$.

Equation of heat balance for the wall separating endothermic and exothermic channels

at z=1, $0 \le \ell \le L$, $T_c = T_w$.

$$\lambda_{z} \frac{\partial T_{c}}{\partial z} + \alpha_{ex} \left(T_{W} - T_{g}^{ex} \right) = w_{CH_{4}O}^{ox} \Delta H_{CH_{4}O} + \lambda_{W} \delta_{W} \frac{d^{2} T_{W}}{d\ell^{2}}.$$

3. Estimation of the model parameters

Rate of CH₄O oxidation in exothermic channels is determined both by intra-diffusion kinetics which is derived from intrinsic kinetics given by (Pasel et al., 2001) and external mass transfer:

$$\omega_{CH_{4}O}^{ox} = \left(\frac{P \times 10^5}{R_g T_g^{ex}}\right) x_{CH_{4}O}^m \frac{k_{CH_{4}O} \beta_{CH_{4}O}^{ex}}{\left(\beta_{CH_{4}O}^{ex} + k_{CH_{4}O}\right)}, \qquad k_{CH_{4}O} = k_{CH_{4}O}^0 \exp\left(\frac{-E_{CH_{4}O}}{R_g T_W}\right),$$

. .

Rate of methanol steam reforming (Peppley et al., 1999)

$$r_{con} = \frac{k_{con} P_{CH_4O} \left[1 - \frac{P_{CO_2} (P_{H_2})^3}{K_e^{con} P_{CH_4O} P_{H_2O}} \right] C_{cat}}{(\sqrt{P_{H_2}} + K_1 P_{CH_4O} + K_2 P_{CO_2} P_{H_2} + K_3 P_{H_2O})(1 + \sqrt{K_4 P_{H_2}})},$$

$$k_{con} = k_{con}^0 \exp\left(\frac{-E_{con}}{R_g T_c}\right), \quad P_i = P y_i^m, \quad i = \{CH_4O, H_2O, CO, CO_2, H_2\},$$

Rate of shift reaction (Peppley et al., 1999)

$$r_{sh} = \frac{k_{sh}\sqrt{P_{H_2}}P_{CO}P_{H_2O}\left(1 - \frac{P_{CO_2}P_{H_2}}{K_e^{sh}P_{CO}P_{H_2O}}\right)C_{cat}}{\left(\sqrt{P_{H_2}} + K_1P_{CH_4O} + K_2P_{CO_2}P_{H_2} + K_3P_{H_2O}\right)^2}, \qquad k_{sh} = k_{sh}^0 \exp\left(\frac{-E_{sh}}{R_gT_c}\right)$$

Rate of methanol decomposition (Peppley et al., 1999)

$$r_{dec} = \frac{k_{dec} P_{CH_4O} \left[1 - \frac{P_{CO} (P_{H_2})^2}{K_e^{dec} P_{CH_4O}} \right] C_{cat}}{(\sqrt{P_{H_2}} + K_5 P_{CH_4O} + K_6 P_{H_2O})(1 + \sqrt{K_7 P_{H_2}})}$$
$$k_{dec} = k_{dec}^0 \exp\left(\frac{-E_{dec}}{R_g T_c}\right), \quad K_n = K_n^0 \exp\left(\frac{-Q_n}{R_g T_c}\right), \quad n = 1, 2, 3...7.$$

Values: E_{con}=82.8 kJ/mole, E_{sh}=67.6 kJ/mole, E_{dec}=150 kJ/mole, E_{CH40}=26 kJ/mole, $k_{con}^0 = 5.6 \times 10^7$, $k_{sh}^0 = 1.6 \times 10^6$, $k_{dec}^0 = 1.6 \times 10^{17}$, $k_{CH40}^0 = 10^4$ m/s, $C_{cal} = 200$ kg/m³.

In experiments were used structured catalysts based on the reinforced porous metal supports. Such supports provide enhanced heat transfer between the exothermic and endothermic zones. Catalyst for methanol steam reforming consists of powdered mixture 38%CuO+ 1.5%Cr₂O₃+27%ZnO/ γ -Al₂O₃ that was supported on the stainless steel net. The alternating flat and corrugated sheets were stacked up to form the desired thickness of the reforming unit. The catalyst for exothermic channels consists of a powdered mixture (79.4%Ni+20%Al+0.6%Pt/ γ -Al₂O₃) which is sintered with a metal wall of the channels. The catalyst preparation technique is described in detail elsewhere (Kirillov et .al., 2003). The coefficients of heat and mass transfer (α , β) between the catalyst and gas in the exothermic and endothermic channels were calculated from the dependencies used in (Kirillov et al., 2004).

4. Results of modeling and experimental testing

The experiments and calculations were performed for the reactor (10 cm length) containing endothermic units (14 mm thickness) with flat and corrugated catalytic stripes (corrugation size is 2-3 mm) and exothermic flat channels (1 mm thickness). The experimental conditions at the endothermic channel inlet were: $y_{CH_3OH}^m = 0.44$; $y_{H_2O}^m = 0.56$; $T_{g0}^{en} = 200^{\circ}$ C; $G_{en} = 0.024$ kg/(m² s). For the exothermic channels, the inlet conditions were: g=3.8 g/(m s); Case 1 (coupling of exo/endo reactions) T $_{go}^{ex} = 100^{\circ}$ C; gas molar content: 77.8%N₂+20.7%O₂+1.5%CH₃OH. Case 2 (preburning): T $_{go}^{ex} = 400^{\circ}$ C; gas molar content: 77.2%N₂+18.3%O₂+3%H₂O+1.5%CO₂. It should be noted that we studied two versions of the process performance in the exothermic channels. The first version represented the oxidation of hydrogen and methanol in the exothermic channels and methanol steam reforming in the endothermic channels.



Fig. 2a,b. Calculated and measured temperature distribution: 1- wall, 2- reforming catalyst (at the plane of symmetry), 3- reforming gas, 4- fuel (or hot) gas; a) case of coupling of endo/exothermic reactions; b) case of preburning of methanol-air mixture.

The second version used an outer catalytic afterburner of anode gases and methanol residues, feeding of the heated reaction products into the exothermic channels and

methanol steam changes in the methanol reforming in the endothermic channels. Fig. 2 shows the calculated results of temperature distribution along the catalyst length.

As follows from Fig. 2 a and b, the maximal temperature is observed at the outlet of the heat-coupled reactor and the general temperature level exceeds that observed for the reactor with a preliminary mixture oxidation. Note that for both versions of the endothermic channel heating, catalyst temperatures measured at a distance of 2-3 cm away from the inlet are very similar, which results in slight differences in the degree of methanol conversion (Fig.3). Since the design and manufacturing of the reactor with a



preliminary mixture mixing are more plain, the main experimental runs were performed using the second reactor version. A comparison of the experimental and calculated data is shown in

Fig. 3. Comparison of theoretical methanol conversion for preburning and heat coupling reactor versions.

Fig 2b (temperatures at the reactor outlet) and Fig. 4 a and b (concentrations of hydrogen, CO and CO_2). Solid lines show the calculated results and dots correspond to the experimental data. The results agree well, which testifies to reliability of the mathematical model and its potentials in calculating methanol reforming reactors.

Fig. 4 a,b. Distributions of CH₄O, H₂, CO and CO₂ molar dry fractions. a) methanol conversion
(1) and H2 molar dry fraction (2).
b) CO and CO₂ molar dry fractions; circle – experiment.
Case of preburning of methanolair mixture.

Acknowledgement

The authors appreciate the ISTC support of this work under Project № 2904.

Nomenclature

 C_{cat} = (volumetric concentration of the catalyst for the reforming unit, kg/m³; c_p^{ex} , c_p^{en} , c_p^j , c_p^i - heat capacity of gas mixture and its components, J/(kg K); α_{en} , α_{ex} - gas-solid heat transfer coefficients in endothermic and exothermic channels, $W/(m^2 K)$; ℓ coordinate along the reactor length, m; z-transverse coordinate, m; $R_g=8.31$ - gas constant, J/(mole K); $\delta_{ex}=0.001$ - height of the exothermic channel, m; $\delta_W=0.001$ thickness of the metallic wall between the channels, m; T - temperature; y_i , x_j - mass fractions of gas components; y_i^m , x_j^m - mole fractions of gas components; G_{en} gas superficial mass velocity in the endothermic channels, kg/(m² s); g- half mass velocity of gas in the exothermic channels, kg/(m s); m_i - mole mass of gas components, - pressure, bar; P_i – partial kg/mole; ΔH_i - heat of reaction, J/mole; P pressure, bar; V_i^j - stoichiometric reaction coefficients; E_i - activation energy J/mole; S - specific catalyst surface, m^2/m^3 ; β - mass transfer coefficient, m/s; $\lambda_z = 1 \text{ W/(m K)}$ - coefficient of heat conductivity.

Subscripts

c, cat - catalyst; *con* - steam conversion of methanol CH₄O; *dec* - reaction of methanol decomposition CH₄O; *m* - mole fraction; *sh* - shift reaction; *H*₂ - hydrogen; ox - reaction of oxidation; *CH*₄O - methanol; *ex* - exothermic channel; *s* - external surface; *g* - gas phase; *i* - gas species in endothermic channel, i = {CH₄O, H₂O, CO, CO₂, H₂} ;j- gas species in exothermic channel, $j = {O_2, N_2, H_2, H_2O, CO_2, CH_4O}$; *W* - wall; *z*- transverse direction.

References

Cao W, G.Chen, S. Li, Q. Yuan, 2006, Chemical Engineering Journal 119, 93. Kirillov, V.A., A.S. Bobrin, N.A. Kuzin, V.A. Kuzmin, A.B. Shigarov, V.B. Skomorokhov, E. I. Smirnov, V.A. Sobyanin, 2004 Ind. & Eng. Chem. Res., 43, 4721. Kirillov, V.A., N.A. Kuzin, A.V. Kulikov, S.I. Fadeev, A.B. Shigarov, V.A. Sobyanin, 2003, Theor. Found. Chem. Eng. 37, 276.

Nagano S., S. Yamamoto, T. Asano, K. Ohsawa, S. Ogino, SAE Technical Paper Series 2002-01-0406.

Lattner J.R. and M.P. Harold, 2005, Applied Catalysis B: Environmental 56, 149.

Reiche A., Foli K., Gronwald O., Haufe S., Kiel S., Maehr U., Melzer D., Walter F., S. Weisshaar. Sartorius HT-PEM Fuel Cell Technology, 2006 Fuel Cell Seminar. November 13-17, 2006. Hawaii, P. 300.

Pazel, J., B. Emonts, R. Peters, D. Stolten, 2001, Catalysis Today 69, 193.

Peppley, B., J. C. Amphlett, L. M. Kearns, R.F. Mann, 1999, Applied Catalysis A: General 179, 31.

Pan L and S. Wang, 2005, International Journal of Hydrogen Energy, 30, 973.