

KINETICS OF OXIDATION OF AMMONIA ON COBALT CATALYST I MODEL OF THE REACTOR WITH CATALYTICALLY ACTIVE WALL

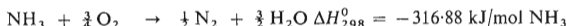
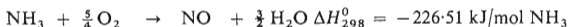
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A two dimensional model of a tubular reactor with the catalytically active wall has been proposed in which several exothermic catalytic reactions take place. The derived dimensionless equations enable evaluation of concentration and temperature profiles on the surface of the active component. The resulting nonlinear parabolic equations have been solved by the method of orthogonal collocations.

In studies of kinetics of strongly exothermic catalytic reactions, which take place at oxidation of ammonia



for investigation of the reaction rates it is not possible to use usual methods. The reason is the considerable reaction rate and large heat of reaction which prevent isothermal performance of the experiment in the integral or differential reactor. Isothermal conditions cannot be reached by dilution of the catalyst, since practically all materials at temperatures above 600°C are catalyzing the oxidation of ammonia to nitrogen. For these reasons the experimental methodics and method of evaluation of the obtained data were searched which would enable determination of kinetic parameters of these reactions in the industrially important region of temperature and concentrations. The most suitable was considered the reactor of circular cross section with internal wall covered by the active component (Fig. 1). In this system it is possible to determine concentrations of components and temperature on the surface of the catalyst from the conversion data by solution of corresponding balance equations describing the concentration and temperature fields in the tube of the reactor.

Majority of studies concerning the tubular reactor with the catalytically active wall (further on TWR — Tubular Wall Reactor) is dedicated to the problem of static modelling¹⁻⁷ or to dynamic behaviour of the reactor⁴ when the kinetics of the considered catalyzed reaction is known. The reverse problem, *i.e.* use of data from TWR for explanation of kinetics, concern⁸⁻¹⁰ only several publications.

Johnstone⁸ has used TWR for studies on low temperature oxidation of ammonia (450 to 490 K on oxidic bismuth-manganese catalysts. The data were evaluated by use of the Damkohler isothermal model¹ at the assumption that the total rate of NH_3 consumption is proportional to the surface concentration of NH_3 .

Cowherd and Hoelschen⁹ used the asymptotic solution by Leveques to the study of kinetics of formation of polyiodides.

Katz¹⁰ pointed to the possibility of use of TWR for studies of catalyzed reactions and derived relations between the mean concentration of components and the form of dependence of the reaction rate on surface concentration.

The problem of TWR is summarised in the study¹¹, where various variants of boundary and initial conditions are considered for the system of first order reactions and analytical solutions of balance equations are given at the assumption of isothermic course of the reaction.

For the system of exothermic catalytic reactions the mathematical description of TWR has not been formulated in any of the already published papers. Derivation of the corresponding model which would include the effect of thermal effects of the reaction on temperature of the wall and would consider variability of transfer coefficients with temperature and composition of the reaction mixture, is the aim of this study.

MATHEMATICAL MODEL

The mathematical model is based on general formulation of the laws of mass and energy conservation. For derivation of final forms of differential equations were

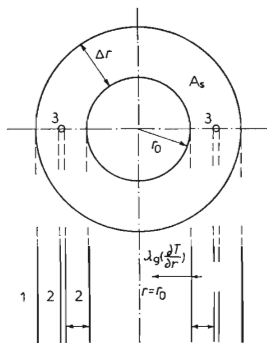


FIG. 1

Cross section of the reactor. 1 Stainless steel block, 2 carrier block (CoAl_2O_4) of the catalytically active component, 3 thermocouple probes

made following simplifications: 1) Molecular mass transfer can be expressed in the form $D_i \nabla \varrho_i$, i.e. validity of the first Fick's law is assumed and the effect of pressure and temperature gradients on diffusion flux are not considered. Similarly for molecular transfer of energy validity of the linear relation between the energy and temperature gradient is assumed (Fourier's law). 2) Energy transfer by radiation is not considered. 3) Quantities D_i , ϱ , λ are constant over the cross sectional area, i.e. in the point z are considered values D_i , ϱ , λ at the mean temperature and composition in the point z . 4) Axial diffusion of components and axial heat transfer in the gaseous phase are neglected. 5) Radial temperature profile in the catalytic block is neglected. 6) The catalytic wall is not porous. 7) No chemical reactions take place in the gaseous phase. 8) Flow of medium through the catalytic tube has a laminar character ($Re < 2000$).

Cross sections of the reactor body and of the catalytic block are demonstrated in Fig. 1.

By making these assumptions for the material and energy balance, equations are obtained

$$G(r) \frac{\partial w_i}{\partial z} - D_i \varrho \left[\frac{1}{r} \frac{\partial}{\partial r} r \left(\frac{\partial w_i}{\partial r} \right) \right] = 0, \quad (1)$$

$$C_p G(r) \frac{\partial T}{\partial z} - \lambda_g \left[\frac{1}{r} \frac{\partial}{\partial r} r \left(\frac{\partial T}{\partial r} \right) \right] = 0. \quad (2)$$

When only the symmetric solutions are considered and when axial heat conduction is neglected, in the Laplace operator there is only one term and for $r = 0$ the relation holds

$$\partial w_i / \partial r = \partial T / \partial r = 0. \quad (3)$$

The boundary conditions for the i -th component can be written in the form

$$D_i \varrho (\partial w_i / \partial r)_{r=r_0} = M_i \sum_k \alpha_{ki} R_k, \quad i = 1, 2, \dots, N \quad (4)$$

or expressed by use of mean (mixing cup) mass fractions, the relation is obtained

$$\left(\frac{\partial w_i}{\partial r} \right)_{r=r_0} = \frac{r_0 \cdot \bar{G}}{2D_i \varrho} \frac{d\bar{w}_i}{dz}. \quad (5)$$

When temperature of the catalytic block in the radial direction is considered to be constant, the enthalpic balance is expressed by equation

$$\lambda_g \left(\frac{\partial T}{\partial r} \right)_{r=r_0} = \sum_k R_k (-\Delta H_k) + \frac{A_s}{2\pi r_0} \lambda_s \frac{\partial^2 T_s}{\partial z^2}. \quad (6)$$

Composition and temperature of the reaction mixture at the inlet into the reactor can be considered to be constant (independent of coordinates r and z)

$$z = 0, \quad w_i(r, 0) = w_i^0, \quad T(r, 0) = T_0. \quad (7)$$

Temperature of the catalytic block in the point $z = 0$ is

$$T_s = T_b^0. \quad (8)$$

DIMENSIONLESS FORM OF BALANCE EQUATIONS

For solution of Eqs (1) and (2) together with boundary conditions (3), (4) and (6) it is suitable to reduce the number of parameters by introduction of dimensionless variables in the above given equations. The independent dimensionless variables are defined by relations

$$y = r/r_0 \quad \text{and} \quad x = (z/r_0)(1/Re Pr). \quad (9)$$

Also the relative mass fractions and dimensionless temperature are introduced

$$\psi_i = w_i/w_i^0 \quad \text{and} \quad \Theta = T/T_0. \quad (10)$$

At the assumption that for a fully developed laminar flow is $G(y) = 2\bar{G}(1 - y^2)$ Eqs (1) and (2) become

$$(1 - y^2) \frac{\partial \psi_i}{\partial x} = \frac{1}{Le_i} \left(\frac{1}{y} \frac{\partial}{\partial y} y \frac{\partial \psi_i}{\partial y} \right) \quad (11)$$

and

$$(1 - y^2) \frac{\partial \Theta}{\partial x} = \frac{1}{y} \frac{\partial}{\partial y} y \frac{\partial \Theta}{\partial y}. \quad (12)$$

Conditions for inlet values of the independent variables ψ_i and Θ (according to Eqs (7) and (8)) are

$$x = 0, \quad \psi_i(y, 0) = \psi_i^0, \quad \Theta = 1, \quad \Theta_s = \Theta_b^0 = T_b^0/T_0. \quad (13)$$

The boundary conditions (4) and (6), by introduction of dimensionless parameters, become

$$\bar{R}_k = R_k/R_1^0, \quad (14)$$

where $R_1^0 = R_1(T_0, w_1^0 \dots w_N^0)$,

$$Da_i = M_i r_0 R_1^0 / D_i \rho w_1^0 \quad (15)$$

$$\delta_k = w_1^0 (-\Delta H_k) / M_1 T_0 C_p \quad (16)$$

$$\beta_s = A_s \lambda_s / 2\pi \lambda r_0^2 (Re Pr)^2 \quad (17)$$

take the form

$$(\partial \psi_i / \partial y)_{y=1} = Da_i \sum_k \alpha_{ki} \bar{R}_k, \quad (18)$$

$$\left(\frac{\partial \Theta}{\partial y}\right)_{y=1} = \sum_k \frac{Da_i}{Le_1} \delta_k \bar{R}_k + \beta_s \frac{\partial^2 \Theta_b}{\partial x^2}. \quad (19)$$

When the boundary condition in the integral form (5) is used the relation is obtained

$$(\partial \psi_i / \partial x)_{y=1} = 0.25 Le_i d\bar{\psi}_i / dx, \quad (20)$$

similarly

$$(\partial \Theta / \partial y)_{y=1} = 0.25 d\Theta / dx, \quad (21)$$

where

$$\bar{\psi}_i(x) = \int_0^1 (1 - y^2) \psi_i(x, y) y dy, \quad (22)$$

$$\bar{\Theta}(x) = \int_0^1 (1 - y^2) \Theta(x, y) y dy. \quad (23)$$

Equations (11), (12), (18), (19) or (20), (21) together with the symmetry relations

$$(\partial \psi_i / \partial y)_{y=0} = (\partial \Theta / \partial y)_{y=0} = 0 \quad (24)$$

form the system of nonlinear parabolic equations where the non-linearities are included in the relations for the reaction rate R_i and (\bar{R}_i) . R_i are in general functions of composition of the reaction mixture in the point $y = 1$ ($r = r_0$) and of temperature of the catalytic surface in this point.

SOLUTION OF EQUATIONS OF THE MATHEMATICAL MODEL

For evaluation of parameters of concrete kinetic models has been necessary to find an effective numerical method for solution of the above given system of nonlinear

parabolic equations which could be used for calculation of the sum of square deviations between the calculated and experimental values ψ_i . The method of orthogonal collocation on finite elements¹⁵⁻¹⁷ was used.

The integration region $0 \leq x \leq x_1$, $0 \leq y \leq 1$ was divided in the direction of the coordinate x into a finite number of intervals Δx_q . On each subregion

$$\sum_{q=1}^Q \Delta x_q \leq x \leq \sum_{q=1}^{Q+1} \Delta x_q, \quad 0 \leq y \leq 1$$

is possible to express the radial component of the approximate solution of Eqs (11) and (12) by use of Lagrange's interpolation polynomials defined on $(M+1)$ collocation points $\{y_j\}_{j=1}^{M+1}$

$$\psi_i^*(x, y) = \sum_{n=1}^{M+1} \psi_i^*(x, y_n) \cdot I_n(y^2), \quad (25)$$

$$\Theta^*(x, y) = \sum_{n=1}^{M+1} \Theta^*(x, y_n) \cdot I_n(y^2), \quad (26)$$

where $I_n(y^2)$ is the n -th Lagrange interpolation polynomial (with the independent variable y^2) of the M -th degree¹⁸. The quantities $\psi_i^*(x, y_n)$ and $\Theta^*(x, y_n)$ are the unknown values of the approximate solution in the radial collocation point y_n .

The set of radial collocation points is chosen so that it should be identical with the nodal points for the Gauss or Radau quadrature. It is then possible to calculate by use of the Gauss (Radau) integration formulas¹⁹, with a high accuracy the mean (mixing cup) values

$$\bar{\psi}_i^*(x) = \sum_{j=1}^{M+1} W_j \cdot \psi_i^*(x, y_j), \quad (27)$$

$$\bar{\Theta}^*(x) = \sum_{j=1}^{M+1} W_j \cdot \Theta^*(x, y_j). \quad (28)$$

By substitution of Eqs (25) and (26) into (11) and (12) the values $\psi_i(x, y)$ and $\Theta(x, y)$ are obtained in radial collocation points $\{y_j\}_{j=1}^{M+1}$

$$\frac{d\psi_i^*(x, y_j)}{dx} = \sum_{n=1}^{M+1} D_{jn}^{(i)} \psi_i^*(x, y_n), \quad (29)$$

$$\frac{d\Theta^*(x, y_j)}{dx} = \sum_{n=1}^{M+1} D_{jn} \Theta^*(x, y_n). \quad (30)$$

The matrices $D^{(1)}$ or D are given by relations

$$D_{jn} = (1 - y_j^2)^{-1} \left[\frac{1}{y} \frac{d}{dy} y \frac{dl_n(y^2)}{dy} \right]_{y=y_j}, \quad (31)$$

$$D_{jn}^{(1)} = Le_i^{-1} D_{jn}, \quad (32)$$

where $j = 1, 2, \dots, M$, $n = 1, 2, \dots, M + 1$.

The boundary conditions (18) and (19) can be written in the form

$$\sum_{j=1}^{M+1} A_{M+1,j} \psi_i^*(x, y_j) = Da_i \sum_k \alpha_{ki} \bar{R}_k, \quad (33)$$

$$\sum_{j=1}^{M+1} A_{M+1,j} \Theta^*(x, y_j) = \sum_k \frac{Da_1}{Le_1} \delta_k \bar{R}_k + \beta_S \sum_{p=1}^L B_{mp} \Theta_b^*(x_p), \quad (34)$$

where

$$A_{kj} = (dl_j(y^2)/dy)_{y=y_k}, \quad B_{mp} = (d^2l_p(x)/dx^2)_{x=x_m}. \quad (35)$$

In the definition (35) is $l_p(x)$ the p -th Lagrange interpolation polynomial of the $(L - 1)$ st degree, defined on the set of axial collocation points $\{x_m\}_{m=1}^L$ in each element Δx_q which is used at discretization of the term $\beta_S \partial^2 \Theta_b / \partial x^2$ in the axial direction.

The integral boundary conditions (20) and (21) can be written by use of Eqs (27) and (28) in the form

$$0.25 Le_i \frac{d}{dx} \sum_{j=1}^{M+1} W_j \psi_i^*(x, y_j) = Da_i \sum_k \alpha_{ki} \bar{R}_k \quad (36)$$

$$0.25 \frac{d}{dx} \sum_{j=1}^{M+1} W_j \Theta^*(x, y_j) = \sum_k \frac{Da_1}{Le_1} \delta_k \bar{R}_k + \beta_S \sum_{p=1}^L B_{mp} \Theta_b^*(x_p). \quad (37)$$

Equations (29) and (30), together with conditions (33) and (34) or (36) and (37), form the system of 1st order differential equations with the given initial condition (13).

With regard to the last term of Eq. (34) or (37) which is bonding the dependent variable $\Theta_b^*(x)$ in the axial direction the given system cannot be solved directly but the iteration procedure must be used *i.e.* on the considered element Δx_q the initial distribution $\Theta_b^*(x)$ is chosen and after integration from x to $x + \Delta x_q$ the newly obtained profile $\Theta_b^*(x)$ is used in the next integration in the same element and this

procedure is repeated till the convergence criteria

$$\sum_{m=1}^L |\Theta_b^{*(p)}(x_m) - \Theta_b^{*(p+1)}(x_m)| < \varepsilon \quad (38)$$

is not satisfied. The values $\Theta_b^{*(p)}(x_m)$ or $\Theta_b^{*(p+1)}(x_m)$ represent estimates of $\Theta_b(x)$ in axial collocation points in the element Δx_q in the p -th or $(p + 1)$ -st iteration.

When the temperature of the wall is given

$$\Theta_b(x) = g(x) \quad (39)$$

then this iteration process is dismissed and integration can be performed directly.

Integration of the initial problem (29) and (30) was performed by the semiimplicit 3rd order method of Runge-Kutta with the automatic selection of the length of the integration step²¹.

Algorithm which included minimisation of the sum of square deviations of experimental and calculated values has been implemented in the language FORTRAN on the computer ICI-4-72 and has been formulated so that it makes possible to evaluate the kinetic parameters of selected rate equations for systems of several reactions from experimental data obtained in the tubular reactor with the catalytically active wall.

Practical application of this method to the case of oxidation of ammonia on the catalyst with the active component Co_3O_4 is the subject of the following study¹⁴.

LIST OF SYMBOLS

- A** matrix for approximation of 1-st derivatives
A_s cross sectional area of the catalytic block (m^2)
B matrix for approximation of 2-nd derivatives
C_p thermal capacity of the gaseous mixture at constant pressure ($\text{J kg}^{-1} \text{K}^{-1}$)
D matrix for approximation of the Laplace operator
D_i effective diffusivity coefficient of component i ($\text{m}^2 \text{s}^{-1}$)
Da_i Damköhler number
G local total mass flux ($\text{kg m}^{-2} \text{s}^{-1}$)
 \bar{G} mean total flux ($\text{m}^{-2} \text{s}^{-1}$)
 $g(x)$ distribution of wall temperature of the catalytic block
 ΔH_i reaction enthalpy of the i -th reaction (kJ mol^{-1})
 $Le_i = \lambda_g / D_i \rho C_p$ Lewis number
 $l_n(x)$ Lagrange's interpolation polynomial
M_i molar weight of the i -th component (kg k mol^{-1})
Pr = $C_p \mu / \lambda_g$ Prandtl number
R_i reaction rate of the i -th reaction ($\text{mol m}^{-2} \text{s}^{-1}$)
 $Re = 2\bar{G}r_0 / \mu$ Reynolds number
 \bar{R}_k dimensionless reaction rate of the k -th reaction
r radial coordinate (m)
r₀ inside diameter of the tubular reactor (m)
T temperature of gas phase (K)

T_s	temperature of solid phase (K)
T_0	temperature of feed (K)
T_b^0	temperature of catalytic block at the inlet (K)
w_i	mass fraction of component i
w_i^0	mass fraction of component i at the inlet into the reactor
\bar{w}_i	mean mass fraction (mixing cup) of component i
W_j	mass coefficient in the Gauss integration formula
$x = (z/r_0)(1/Re Pr)$	dimensionless axial coordinate
$y = (r/r_0)$	dimensionless radial coordinate
z	axial coordinate (m)
α_{ij}	matrix of stoichiometric coefficients
β_s	parameter defined by Eq. (17)
δ_i	dimensionless adiabatic temperature increase defined by Eq. (16)
ψ_i	relative mass fraction of i -th component
ψ_i^0	relative mass fraction of i -th component at the inlet
$\bar{\psi}_i$	mean (mixing cup) value
θ	dimensionless temperature of gaseous phase
θ_b	dimensionless temperature of solid phase
θ_b^0	dimensionless temperature of solid phase at the inlet
$\bar{\theta}$	mean (mixing cup) value
ψ_i^*	approximate solution corresponding to ψ_i
θ^*	approximate solution corresponding to θ
ρ	density of the gaseous mixture (kg m^{-3})
μ	dynamic viscosity of the gaseous mixture ($\text{kg m}^{-1} \text{s}^{-1}$)
λ_g	thermal conductivity of the gaseous mixture ($\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$)
λ_s	thermal conductivity of the solid phase ($\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$)

Subscripts

g	related to gaseous phase
s	related to solid phase
o	inlet values

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