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Simplified Treatment of Mass Transfer for Gas-Phase Hydrogenation/Dehydrogenation of Heavy Compounds

Alexey B. Shigarov, Stanislav I. Fadeev*, Irina A. Mikhailova, Alexander V. Kulikov,
Victor K. Korolev*, Nicolay A. Kuzin and Valery A. Kirillov†

Boreskov Institute of Catalysis, Prosp. Akad. Lavrentieva 5,
*Sobolev Institute of Mathematics, Prosp. Akad. Koptyuga 4, 630090, Novosibirsk, Russia

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Abstract–Using single catalyst pellets (5 mm) 15% Pt/γ-Al_2O_3, we experimentally studied gas-phase benzene hydrogenation at normal pressure by thermocouple measurements of gas flow and the pellet center. Temperature of gas flow was varied in the range of 20 °C : 350 °C for three molar fractions of benzene vapor (0.1, 0.2, and 0.3) mixed with hydrogen. The ignition/extinction behavior of the flow-pellet temperature rise (maximum values up to 100 °C : 200 °C) is explained by internal-external mass transport limitations of the reaction rate and reaction reversibility at high pellet temperature. A simplified pseudobinary treatment of both multicomponent intrapellet mass transfer (in bimodal porous media) and multicomponent external mass transfer (under forced convection) is proposed on the basis of the analytical estimation. The validity of the suggested approach is confirmed by comparing the experimental data for benzene hydrogenation with rigorous (multicomponent) and approximated (pseudobinary) calculations obtained by using a mathematical model of a spherically symmetric pellet. The simplified approach appears to be quite accurate for reactions $A+nH_2=B$ of hydrogenation ($n>0$) or dehydrogenation ($n<0$) of sufficiently heavy compounds, i.e. if $D_{AH}\approx D_{BH}>>D_{AB}$.

Key words: Gas Phase Benzene Hydrogenation, Flow-Catalyst Pellet Temperature Rise, Multicomponent and Binary Diffusion, Internal and Interphase Mass and Heat Transfer

INTRODUCTION

The problems of hot spots and runaway are significant for industrial reactors with a fixed catalyst bed for hydrocarbon hydrogenation and refer both to gas-phase multitube reactors and liquid-phase, usually trickle-bed, reactors [Goossens et al., 1997]. The study of the vapour phase reaction proceeding on the completely dry catalyst pellets is the starting point for understanding these abnormal phenomena. There is a lack of experimental and theoretical research of this simple, from the traditional point of view, problem. This fact may be attributed to the multicomponent nature of mass transport processes in mixtures with hydrogen and, consequently, to the necessity of applying cumbersome mathematical techniques [Khadilkar et al., 1999] instead of the traditional binary (Fick) approach. Although the Maxwell-Stefan equations describing the internal/external mass transfer are rather elegant and general [Krishna and Wesselingh, 1997], many attempts have been made to reduce the multicomponent problem to a binary one for particular industrially important cases [Eddings and Sohn, 1993]. Other questions arise for the gas-phase internal diffusion models with bimodal porous size distribution of catalyst support [Haugaard and Livbjerg, 1998].

Benzene hydrogenation serves as a model reaction. Besides, this reaction is important for industry and is a typical example of hydrocarbon hydrogenation reactions. This class of reactions is characterised by a considerable heat effect and fast intrinsic kinetics. In addition, if the reaction proceeds in the presence of highly active catalysts and high pressure, both internal and external diffusion resistance may affect apparent rate of the gas-phase reaction. In the latter case, the catalyst may undergo significant temperature rise with respect to gas flow (hundreds of degrees). It is important to determine the value of such flow-pellet temperature difference in order to avoid unwanted side processes resulting in deactivation of catalyst. In some cases one should know the apparent rate of the reaction occurring on the catalyst pellet under transport limitations (external, internal or transition). To answer the question, the following data are required: (1) intrinsic kinetics, (2) intrapellet heat and mass transfer, and (3) interphase (gas-solid) heat and mass transfer. Here we consider problems concerning only the last two items.

According to [Malinovskaya et al., 1975], a simple homogeneous porous diffusion model cannot be directly used for a general case of the bidispersed porous catalyst structure. For monoporous catalysts with pore size radius, which corresponds to transition between Knudsen and molecular diffusion, the Dusty Gas Model is commonly accepted [Mason and Malinauskas, 1983]. This model is sometimes used for a wider range, e.g. for macropores [Papavassiliou et al., 1997]. But for free molecular diffusion in the porous medium, which is typical for processes under pressure and/or in the presence of macroporous catalysts, it is more convenient to use the Stefan-Maxwell multicomponent diffusion model [Frank-Kamenetskii, 1955], corrected for medium permeability. Krishna [1993] noted that the majority of works, concerning the pore diffusion in catalysts, are based on Fick's law, which is, strictly speaking, true only if all binary diffusion coefficients are close and for binary or diluted mixtures.

As far as the internal diffusion is concerned, reduction of multicomponent equations to binary diffusion (Fick's law) is not of principal importance, but it allows a significant simplification of the calculation method and a possibility of analytic estimations. The things

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†To whom correspondence should be addressed.
E-mail: V.A.Kirillov@catalysis.nsk.su

are different with the external mass and heat transfer under forced convection conditions. An application of traditional empirical correlations for gas-solid transfer, based on Chilton-Colburn analogy, implies that physical properties of a mixture undergo insignificant variation within the boundary layer and, so, may be easily averaged. However, for vapor-phase hydrocarbon hydrogenation or dehydrogenation the coefficients of binary diffusion and component heat conductivity in a ternary mixture (hydrogen and two hydrocarbons) may differ by more than an order of magnitude. General approaches for the interphase multicomponent mass transfer have been developed [Stewart and Prober, 1964; Toor, 1964; Taylor and Krishna, 1993]. These methods are still not popular among chemical engineers. Besides, their application for the gas-phase convection transfer is not strictly justified, because thickness of the diffusion film is not known. Excepting the early works on the catalytic hydrogen oxidation on Pt-wire [Buben, 1946] and cyclohexane dehydrogenation in the catalyst bed [Graham et al., 1968], we have not found any experimental testing of interphase transfer models for gas-phase hydrogenation/dehydrogenation reactions under conditions of strong external transport limitations. Our recent paper [Kirillov et al., 2000] considers both experimentally and theoretically the case of heterogeneous gas-phase hydrocarbon hydrogenation under conditions of external transport control and the irreversible reaction. Hydrogenation of alpha-methylstyrene and octene on a single catalyst pellet has verified the originally developed approach (we named it as pseudobinary). This simplified treatment of mass transfer is especially attractive for (de)hydrogenated multicomponent mixtures when a general multicomponent approach seems to be too cumbersome from the engineering standpoint.

The aim of this paper is to generalize the simplified treatment of mass transfer in reversible (de)hydrogenation reactions with possible internal transport limitations and to compare the pseudobinary and multicomponent modelling and the experimental data for the gas-phase benzene hydrogenation.

EXPERIMENTAL

Using a single spherical catalyst pellet (15% Pt/Al_2O_3) 5 mm in diameter, we studied the gas phase benzene hydrogenation at normal pressure by thermocouple measurements of gas flow and the pellet center (Fig. 1). Experimental setup is similar to that, employed in [Kirillov et al., 2000]. The gas flow temperature was varied in the range 20-350 °C for three molar fractions of benzene vapour (0.1, 0.2 and 0.3) mixed with hydrogen. The ignition/extinction behaviour type of the flow-pellet experimental temperature rise (filled triangles in Fig. 3) is explained by internal-external mass transport limitations, existence of maximum intrinsic rate and reaction reversibility at high pellet temperatures.

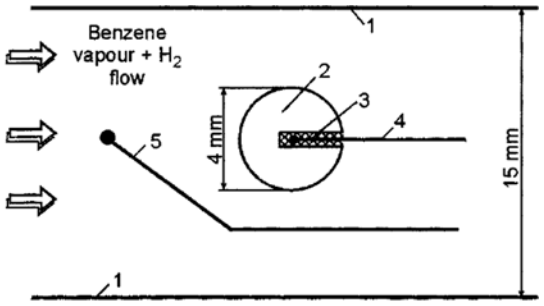

Fig. 1. Scheme of temperature measurements.

1. Quartz wall tube
2. Spherical catalyst pellet
3. Channel (0.5 mm in. diam.), filled by catalyst powder and silicate glue mixture
4. Thermocouple for measuring temperature at the pellet center
5. Thermocouple for measuring gas flow temperature

BIMODAL POROUS STRUCTURE AND QUASI-HOMOGENEOUS MODEL

1. Characteristics of the Catalyst Porous Structure

The catalyst dispersion (fraction of surface atoms in Pt crystallites) was about 50%. According to X-ray analysis, the average size of Pt crystallites was 17-20 A. The specific surface area of all pores was 206 m^2/g and the specific pellet density was 0.72 g/cm^3. According to mercury porosimetry, the total pore volume was 0.75 cm^3/g. The volume of micropores (r_p<100 A), mesopores (100 A< r_p<1,000 A) and macropores (r_p>1,000 A) was, respectively, 0.5, 0.05 and 0.2 cm^3/g. Pore radius distribution (Fig. 2) has two maximums. One is situated in the region of macropores ($r_p \approx 5{,}000$ A). According to the data on low-temperature nitrogen adsorption, the second maximum for micropores was at $r_p \approx 50$ A. Therefore, the catalyst structure was close to the bidispersion type. Idealizing the actual picture of continuous size pore distribution, we assume that the catalyst structure is described by a bidispersion globule model [Ruthven, 1984]. For such idealization the fraction of macropores ($r_a \approx 5{,}000$ A) is $\varepsilon_a=0.18$ of the pellet volume and that of micropores ($r_i \approx 50$ A) is $\varepsilon_{ii}=0.36$. The total pellet porosity is $\varepsilon_{tot}=\varepsilon_a+\varepsilon_{ii}=0.54$. Macropores are formed by a free space between spherical macro globules. According to [Malinovskaya et al., 1975], the radius of macro globules can be assumed as $R_a \approx 10 r_a = 5$ μm. Micropores are situated inside of such macro globules. The porosity of macro globules is $\varepsilon_i=\varepsilon_{ii}/(1-\varepsilon_a) \approx 0.44$. The tortuosity coefficient of micro and macropores is assumed to be $\tau=3$ as for perfect isotropic porous media [Johnson and Stewart, 1965]. Consequently, the coefficient of pellet macroporous permeability is $p_a=\varepsilon_a/\tau \approx 0.06$. The coefficient of macroglobules microporous permeability is $p_i=\varepsilon_i/\tau \approx 0.15$.

2. Characteristics of Gas Diffusion in Micro and Macro Pores

The mean free path L_A of a benzene molecule in a 10% mixture

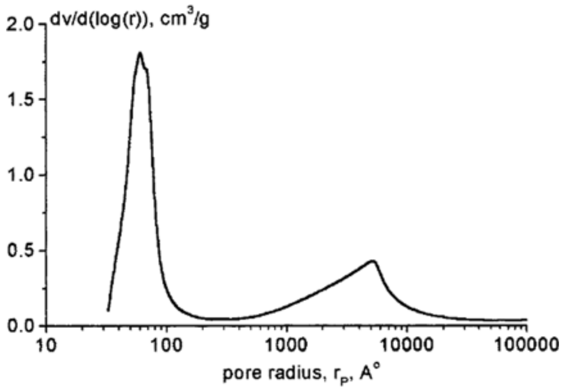

Fig. 2. Pore radius distribution for catalyst 15%Pt/γ-Al_2O_3.

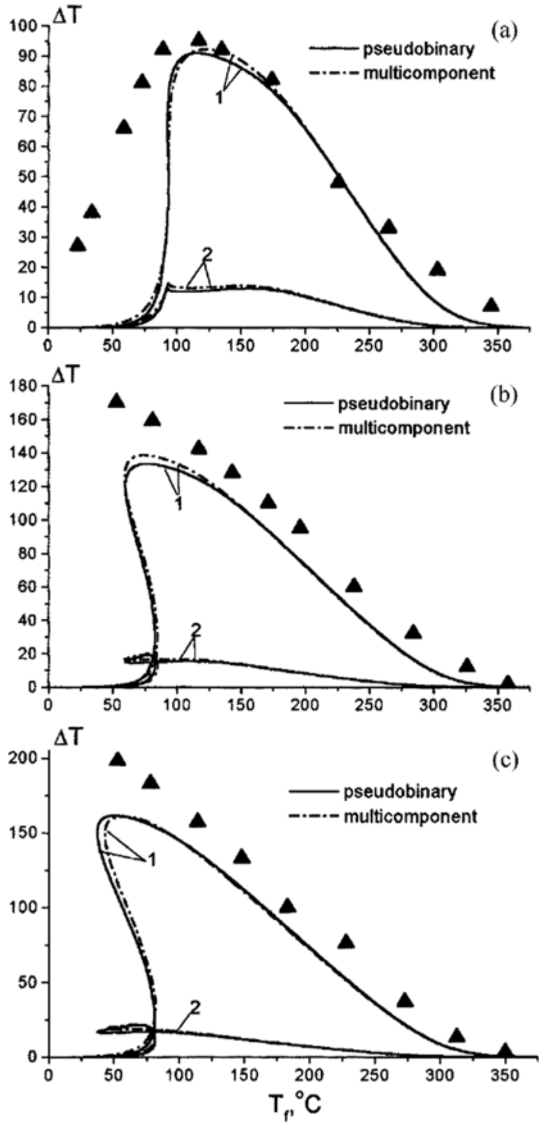

Fig. 3. Comparison of experimental (triangles) with calculated interphase (flow-pellet center) temperature rise ΔT_{cf}=T(0)–T_f (curve 1) and intrapellet (surface-pellet center) temperature rise ΔT_{cs}=T(0)–T(R) (curve 2) dependence on gas flow temperature T_f for different benzene vapor molar fractions in gas flow mixture with H_2: x_{Af}=0.1 (a), x_{Af}=0.2 (b), x_{Af}= 0.3 (c).

of benzene and 90% hydrogen is determined by the Maxwell formula [Malinovskaya et al., 1975]:

$$L_A = \frac{1}{\pi C_t N_{AV}(x_A d_A^2\sqrt{2} + x_H d_H^2\sqrt{1+m_A/m_H})},$$

where the diameter of benzene and hydrogen molecules is, respectively, d_A=5 A and d_H=1.5 A, $N_{AV}=6\times10^{23}$. It follows that L_A=800-1,300 A in the temperature range of 300-500 K at normal pressure. This means that $L_A/2r_i\sim10$ and $2r_a/L_A\sim10$. Therefore, in further discussion we may assume that in micropores Knudsen diffusion occurs and in macro pores - free-molecular diffusion. High pressure in the industrial reactors also weakens the influence of Knudsen diffusion in macropores.

3. Knudsen Diffusion in Micropores

The coefficient of Knudsen diffusion in a channel [Jackson, 1977] is:

$$D^K = \frac{2}{3} r_p \sqrt{\frac{8R_gT}{\pi m}}.$$

For hydrocarbons hydrogenation/dehydrogenation we usually have the relation:

$$\frac{D_A^K}{D_H^K} = \sqrt{\frac{m_H}{m_A}} << 1.$$

So, it is reasonable to assume that the reaction rate in micropores should be limited by diffusion of the heavy reagent (benzene). Estimating the coefficient of Knudsen diffusion for benzene in a micropore r_i=50 A at 200 °C, one has 1.3×10^{-6} m²/s. Taking into account the correction for permeability of macroglobules with Knudsen pores, the effective coefficient of benzene diffusion inside macroglobules will be as:

$$p_i D_A^K \approx 2\times10^{-7}\ \mathrm{m^2/s}.$$

4. Effectiveness Factor for Macroglobules

In order to show that the effectiveness factor is always close to unity (in our case), it will be sufficient to check that a reaction proceeds without transport limitation (regarding the macroglobule scale) under conditions of kinetic maximum at 210 °C. Following [Ostrovskii et al., 1991], we propose that the reaction is of first order with respect to benzene at the kinetic maximum point. Then, the effective depth of reaction penetration into the macroglobule [Frank-Kamenetskii, 1955] will be

$$h = \sqrt{\frac{p_i D_A^K}{k_{max}}}.$$

Recalculating the kinetic data at T=210 °C [Ostrovskii, 1991] for our platinum catalyst (the concentration of Pt is increased by a factor of 30 and dispersion is decreased by 30%), and assuming that the reaction is structurally insensitive, we get $k_{max}\approx90$ 1/s. In this case, h≈45 μm, which is about an order of magnitude higher than the radius of macroglobules $R_a\approx5$ μm. This indicates that the benzene concentration and, consequently, the reaction rate along the length of Knudsen pores (inside of macroglobules) change insignificantly for the considered conditions. So, the effectiveness factor for macroglobules is always close to unity (in our case) An account of surface diffusion in micropores can only confirm the above estimation.

Therefore, it is justified to use a quasi-homogeneous mathematical model of mass transfer inside the porous catalyst pellet with a bimodal porous structure, implying molecular diffusion in macropores in the absence of diffusion resistance in micropores.

ANALYTICAL ESTIMATIONS OF MULTICOMPONENT AND PSEUDOBINARY DIFFUSION MODELS

Let us consider a reaction of gas-phase hydrogenation (n>0) or dehydrogenation (n<0).

$$A + nH_2 = B \qquad (1)$$

The Maxwell-Stefan equations [Frank-Kamenetskii, 1955] take the form:

$$C_t\frac{dx_A}{dr}=\frac{x_AN_H-x_HN_A}{D_{AH}}+\frac{x_AN_B-x_BN_A}{D_{AB}}, \tag{2}$$

$$C_t\frac{dx_B}{dr}=\frac{x_BN_H-x_HN_B}{D_{BH}}+\frac{x_BN_A-x_AN_B}{D_{AB}}, \tag{3}$$

$$C_t\frac{dx_H}{dr}=\frac{x_HN_A-x_AN_H}{D_{AH}}+\frac{x_HN_B-x_BN_H}{D_{BH}}, \tag{4}$$

For external diffusion mass transfer, r will be considered as the co-ordinate across the diffusion film (gas boundary layer around the catalyst pellet), and D_{AH}, D_{BH} and D_{AB} will be considered as the coefficients of molecular binary diffusion D^M_{AH}, D^M_{BH}, D^M_{AB}. In case of internal diffusion mass transfer for a symmetric catalyst pellet (plate, cylinder, sphere), r is the co-ordinate with respect to radius, and $D_{AH}=p_aD^M_{AH}$, $D_{BH}=p_aD^M_{BH}$, $D_{AB}=p_aD^M_{AB}$ are the effective coefficients of molecular binary diffusion through the porous medium of the specified permeability p_a=const. From the conditions of pellet symmetry and stoichiometry of reaction (1), the molar fluxes are related as:

$$N_H=nN_A,\ N_A=-N_B \tag{5}$$

Summing up linearly dependent Eqs. (2)-(4), we obtain the balance relation:

$$x_A+x_B+x_H=1. \tag{6}$$

Using Eqs. (5)-(6), the Maxwell-Stefan Eqs. (2)-(4) can be written as:

$$N_A=-C_tD_A\frac{dx_A}{dr}, \tag{7}$$

$$N_B=-C_tD_B\frac{dx_B}{dr}, \tag{8}$$

$$N_H=-C_tD_H\frac{dx_H}{dr}, \tag{9}$$

The effective diffusion coefficients of each component depend on the mixture composition:

$$\frac{1}{D_A}=\frac{x_H-nx_A}{D_{AH}}+\frac{1-x_H}{D_{AB}}, \tag{10}$$

$$\frac{1}{D_B}=\frac{x_H+nx_B}{D_{BH}}+\frac{1-x_H}{D_{AB}}, \tag{11}$$

$$\frac{1}{D_H}=\frac{nx_A-x_H}{nD_{AH}}+\frac{nx_B+x_H}{nD_{BH}}, \tag{12}$$

Consider the case of (de)hydrogenation of sufficiently large (e.g. hydrocarbon) molecule A, which converts to B by scheme (1). In this case binary diffusion coefficients of the reagent and product with hydrogen are close and significantly exceed the binary coefficient of mutual diffusion between the reagent and product:

$$D_{AH}\approx D_{BH}>>D_{AB}. \tag{13}$$

We shall show below that if condition (13) is satisfied, the multicomponent diffusion Eqs. (7)-(12) have an approximation in the form of equations for binary diffusion of A and B at x_H=const and $D_*(x_H)$=const.

Dividing Eq. (9) by Eq. (7) and using Eq. (5), we get the differential equation for a variation in hydrogen fraction:

$$\frac{dx_H}{dx_A}=\frac{N_HD_A}{N_AD_H}=\frac{nD_A}{D_H}. \tag{14}$$

Substitution of Eqs. (10) and (12) into Eq. (14) rearranges it to

$$\frac{dx_H}{dx_A}=\frac{n(1-x_H)+\varepsilon(x_H+nx_B)}{1+S(1-x_H)-nx_A}, \tag{15}$$

which includes two dimensionless parameters:

$$S=\frac{D_{AH}}{D_{AB}}-1=\frac{D_{AH}-D_{AB}}{D_{AB}}, \tag{16}$$

$$\varepsilon=\frac{D_{AH}}{D_{BH}}-1=\frac{D_{AH}-D_{BH}}{D_{BH}}, \tag{17}$$

Using the inequalities obtained from balance Eq. (6)

$$x_A\le 1-x_H,\ x_B\le 1-x_H,\ |x_H+nx_B|\le x_H+|n|(1-x_H)\le|n|,$$
$$|S(1-x_H)-nx_A|\ge|S|(1-x_H)-|n|x_A\ge(|S|-|n|)(1-x_H),$$

and employing Eq. (15), we get the upper estimation for a variation in hydrogen fraction in the differential form:

$$\left|\frac{dx_H}{dx_A}\right|\le\frac{|n|[(1-x_H)+\varepsilon]}{1+(|S|-|n|)(1-x_H)}\le\varepsilon_H, \tag{18}$$

$$\varepsilon_H=\max\left[\varepsilon|n|,\ \frac{|n|}{|S|-|n|}\right]. \tag{19}$$

In the integral form, the estimation (18) can be written as:

$$|\Delta x_H|\le\varepsilon_H|\Delta x_A|. \tag{20}$$

If for the reaction of hydrocarbon (de)hydrogenation (1), condition (13) is satisfied, then according to Eqs. (16), (17), (19):

$$S>>1,\ |\varepsilon|<<1,\ \varepsilon_H<<1, \tag{21}$$

that is, hydrogen fraction remains practically constant. For the limiting case at $\varepsilon_H=0$, hydrogen can be considered as an inert mixture component:

$$x_H=\text{const},\ N_H=0. \tag{22}$$

Substituting Eqs. (22) into the Maxwell-Stefan Eqs. (2)-(3), one gets the equations for pseudobinary diffusion of reagent A and product B in the presence of inert hydrogen:

$$N_A^*=-C_tD_*\frac{dx_A^*}{dr}=-N_B^*=C_tD_*\frac{dx_B^*}{dr}, \tag{23}$$

where the effective coefficient of pseudobinary diffusion does not depend on coordinate r:

$$\frac{1}{D_*}=\frac{x_H}{D_{AH}}+\frac{1-x_H}{D_{AB}}. \tag{24}$$

Let us estimate the value of error appearing on changing the equations for multicomponent diffusion (7)-(12) to equations for pseudobinary diffusion (23)-(24). For this purpose, Eq. (23) is divided by Eq. (7) and then Eqs. (10) and (24) are substituted into the resulting expression:

$$\frac{N_A^*dx_A}{N_Adx_A^*}=\frac{D_*}{D_A}=\frac{(x_H-nx_A)/D_{AH}+(1-x_H)/D_{AB}}{x_H/D_{AH}+(1-x_H)/D_{AB}}. \tag{25}$$

Suppose that the molar flux of reagent A is known $N_A=N_A^*$, then the approximation error (on defining the gradient of molar fraction A) is estimated from Eq. (25) as:

$$\varepsilon_A = \left|1 - \frac{dx_A}{dx_A^*}\right| = \left|1 - \frac{D_*}{D_A}\right| = \left|\frac{nx_A}{1+S(1-x_n)}\right| \le \frac{|n|}{S}. \tag{26}$$

Note that the above estimations are not a rigorous ground for reducing the multicomponent diffusion equations to pseudobinary Eqs. (23)-(24). Meanwhile, Eqs. (18)-(20) for estimation of hydrogen fraction variation are valid for any arbitrary reaction kinetics. Estimation (26), though is not so general as (18)-(20) but is also interesting because it shows that the value of effective multicomponent diffusion coefficient D_A, determined by Eq. (10), is practically constant if S>>1. Note that at this condition, the coefficient of pseudobinary diffusion D_* in Eq. (24) is an approximation for D_A. A similar conclusion is true for the effective coefficient of multicomponent diffusion D_B from Eq. (11):

$$D_A \approx D_B \approx D_* \quad \text{at } S>>1.$$

Detailed analysis shows that D_* is the lower approximation of D_A with maximum deviation ε_A [Eq. (26)] for hydrogenation reactions (n>0), and D_* is the upper approximation for dehydrogenation reactions (n<0) with the same maximum deviation ε_A.

The physical meaning of the above estimations is that the effective coefficient of hydrogen diffusion is much higher than those of relatively heavy hydrocarbons (reagent A and product B) in the three-component gas mixture. For this reason hydrogen can be treated as an inert component with an infinitely large diffusion coefficient. The properties of A and B molecules are rather close. Diffusion of A and B in ternary mixture (A, B, H) reduces to pseudobinary diffusion of A and B between themselves. The effective coefficient from Eq. (24) depends significantly on the hydrogen fraction x_H= const. Note that total molar flux (arising from change in number of moles during chemical reaction) should not be taken into account in case of such pseudobinary treatment.

Although Eq. (24) looks like the Wilke formula [Wilke and Lee, 1955], its physical meaning is different. The Wilke formula is derived from the Maxwell-Stefan equations for the component diffusing through a stagnant (or strongly diluted) mixture. The things are different in our case.

Note that the coefficient of pseudobinary diffusion D_* in Eq. (24) does not depend on the stoichiometric coefficient n. In contrast to the effective multicomponent diffusion coefficients (10)-(12), D_* describes the physical property of mixture (A, B, H) providing condition (13) holds. This means that Eq. (24) can be experimentally tested by using diffusion measurements (without a chemical reaction). The physical meaning of Eq. (24) is especially clearly seen if the hydrogen fraction in the mixture is close to the vapour fraction $x_H \sim (1-x_H)$. According to condition (13) $D_{AH} >> D_{AB}$, and, consequently, diffusion resistance from hydrogen can be neglected:

$$\frac{x_H}{D_{AH}} << \frac{1-x_H}{D_{AB}}.$$

In this case, the coefficient of pseudobinary diffusion (24) is equivalent to the coefficient of usual binary diffusion of heavy components A and B, if their total pressure $P_{AB}=P_A+P_B=P-P_H$ is varied by hydrogen partial pressure:

$$D_* \approx \frac{D_{AB}}{1-x_H} = D_{AB}\left(\frac{P}{P_{AB}}\right),\ P_i = Px_i,\ (i = A, B, H). \tag{27}$$

Therefore, the above estimations substantiate the approximation of multicomponent diffusion equations for the reactions following scheme (1) with the constraint (13) to Eqs. (23)-(24) describing the so-called pseudobinary diffusion. This permits one to significantly simplify calculations of internal diffusion mass transfer in the case of free-molecular diffusion in the catalyst pores, but, what is more important, this provides reliable grounds for applying the traditional empirical correlations, based on Chilton-Colburn analogy, for interphase gas-solid transfer under forced convection conditions. For the reaction of gas-phase hydrogenation of benzene into cyclohexane

$C_6H_6+3\ H_2=C_6H_{12}$,

which follows the scheme (1) at $A=C_6H_6$; $B=C_6H_{12}$; n=3, the values of binary diffusion coefficients at T=293 K [Reid et al., 1987] are $D_{AH}=3.50\times10^{-5}$ m^2/s, $D_{BH}=3.35\times10^{-5}$ m^2/s, and $D_{AB}=0.27\times10^{-5}$ m^2/s. Thus, condition (13) is qualitatively satisfied. Eqs. (16), (17), (19) and (26) give S=12, ε=0.05, ε_H=0.33, and ε_A=0.25. Therefore, the estimations predict that the pseudobinary method provides a moderate accuracy as compared to the multicomponent method in case of benzene hydrogenation.

MATHEMATICAL MODELS

The aim of mathematical modeling was to verify the analytical estimations, obtained in the previous section, concerning the approximation of the multicomponent mass transfer model (by pseudobinary model) and to compare the calculated and experimental results. To describe internal mass transfer, we used two multicomponent models: 1) the Dusty Gas, 2) Maxwell-Stefan, and 3) pseudobinary model. For gas-solid interphase mass transfer, two additional variants of boundary conditions were used: 4) multicomponent model [Stewart and Prober, 1964; Toor, 1964] and 5) pseudobinary model. The heat transfer equations (both for interphase and intrapellet transfer) were the same for all mass transfer versions.

Equations of continuity and conductive heat transfer inside the spherically symmetric catalyst pellet:

$$\frac{d}{dr}(r^2N_i) = r^2\nu_i W,\ i = A, B, H,\ \nu_A = -1,\ \nu_H = -1,\ \nu_B = 1,$$

$$0 \le r \le R,\ R = 2\times10^{-3}\ \text{m}.$$

$$\frac{d}{dr}\left(r^2\lambda_p \frac{dT}{dr}\right) = -r^2 Q_r W,\ \lambda_p = 0.2\ \text{W/(m K)},$$

1) **The Dusty Gas relations** for intrapellet mass transfer:

$$C_t\frac{dx_i}{dr} = \sum_{j=A,B,H,j\ne i} \frac{x_iN_j - x_jN_i}{p_aD_{ij}} - \frac{N_i}{D_i^K} - \frac{x_i}{R_gT}\left(\frac{B_0P}{\mu D_i^K}+1\right)\frac{dP}{dr},\ i = A, B, H,$$

$$\sum_{i=A,B,H}\frac{N_i}{D_i^K} = -\frac{1}{R_gT}\left(1+\frac{B_0P}{\mu}\sum_{i=A,B,H}\frac{x_i}{D_i^K}\right)\frac{dP}{dr},$$

$$C_t = \frac{P}{R_gT},\ D_i^K = \frac{4}{3}K_0\sqrt{\frac{8R_gT}{\pi m_i}};\ K_0 = \frac{\varepsilon_a r_a}{2\tau};\ B_0 = \frac{\varepsilon_a}{\tau}\left(\frac{R_a^2}{45}\right)\left(\frac{\varepsilon_a}{1-\varepsilon_a}\right),$$

$$R_a = 10r_a,\ \tau = 3,\ \varepsilon_a = 0.18,\ r_a = 5\times10^{-7}\ \text{m},\ p_a = 0.06,$$

$$D_{AH} = 3.5\times10^{-5}\left(\frac{T}{300}\right)^{1.9}\ \text{m}^2/\text{s},\ D_{AB} = 0.27\times10^{-5}\left(\frac{T}{300}\right)^{1.9}\ \text{m}^2/\text{s}.$$

2) **The Maxwell-Stefan relations** for intrapellet mass transfer:

$$C_t\frac{dx_i}{dr}=\sum_{i=A,B,H,j\neq i}\frac{x_iN_j-x_jN_i}{p_aD_{ij}},\ P=\mathrm{const}=10^5\ \mathrm{Pa},\ i=A,\ B,\ H,$$

3) **The pseudobinary relations** for intrapellet mass transfer:

$$N_A=-D_pC_t\frac{dx_A}{dr},$$

$$x_B=1-x_A-x_H,\ x_H=x_{Hf}=\mathrm{const},$$

$$D_p=p_aD_*,\ D_*=[x_H/D_{AH}+(1-x_H)/D_{AB}]^{-1}.$$

Boundary conditions for all versions of interphase mass transfer

$$r=0:\ \frac{dT}{dr}=0;\ N_i=0,\ i=A,\ B,\ H,$$

$$r=R:\ \lambda_p\frac{dT}{dr}=\alpha(T_f-T),$$

4) **Additional boundary conditions for multicomponent interphase mass transfer** [Stewart and Prober, 1964; Toor, 1964] if $D_{AH}=D_{BH}$:

$$r=R:$$

$$N_H=C_{tf}\beta_{AH}(x_H-x_{Hf})+x_{Hf}\sum_{i=A,B,H}N_i,$$

$$N_A=C_{tf}\beta_{AH}\left[\frac{\beta_*}{\beta_{AH}}(x_A-x_{Af})-\left(1-\frac{\beta_*}{\beta_{AH}}\right)\frac{x_{Af}}{1-x_{Hf}}(x_H-x_{Hf})\right]+x_{Af}\sum_{i=A,B,H}N_i,$$

$$N_B=C_{tf}\beta_{AH}\left[\frac{\beta_*}{\beta_{AH}}(x_B-x_{Bf})-\left(1-\frac{\beta_*}{\beta_{AH}}\right)\frac{x_{Bf}}{1-x_{Hf}}(x_H-x_{Hf})\right]+x_{Bf}\sum_{i=A,B,H}N_i,$$

$$C_{tf}=\frac{P}{R_gT_f},\ \beta_*=\frac{Sh_*D_*}{2R},$$

5) **Additional boundary conditions for pseudobinary interphase mass transfer** treatment (at the external surface of the pellet):

$$r=R:\ C_tD_p\frac{dx_A}{dr}=\beta_*C_{tf}(x_{Af}-x_A).$$

Gas-solid mass and heat transfer correlations are taken following [Hugmark, 1967]:

$$Sh_*=2+0.6Re^{0.5}Sc_*^{0.33},\ \beta_{AH}=\frac{Sh_{AH}D_{AH}}{2R},\ Sh_{AH}=2+0.6Re^{0.5}Sc_{AH}^{0.33},$$

$$Sc_*=\frac{\mu}{D_*\rho},\ Sc_{AH}=\frac{\mu}{D_{AH}\rho},\ \rho=C_{tf}(x_Am_A+x_Hm_H),\ Re=\frac{2RG}{\mu},$$

$$G=\frac{V_HG_m\left(m_H+\frac{x_{Af}}{x_{Hf}}m_A\right)}{\pi d_t^2/4},\ d_t=15\times10^{-3}\ \mathrm{m},\ C_m=\frac{P}{R_g\times293},$$

for $x_{Af}=0.1$: $V_H=78.3\times10^{-6}\ \mathrm{m^3/s}$,
$x_{Af}=0.2$: $V_H=34.8\times10^{-6}\ \mathrm{m^3/s}$,
$x_{Af}=0.3$: $V_H=20.3\times10^{-6}\ \mathrm{m^3/s}$,

$$\mu=0.77\times10^{-5}\left(\frac{T_f}{300}\right)^{0.75}\ \mathrm{(N\ s)/m^2},\ m_A=78\times10^{-3}\ \mathrm{kg/mole},$$

$$m_H=2\times10^{-3}\ \mathrm{kg/mole},$$

$$\alpha=\frac{Nu\lambda}{2R},\ Nu=2+0.6Re^{0.5}Pr^{0.33},\ Pr=\frac{\mu c_pC_t}{\lambda},$$

$$c_p=c_{pA}x_{Af}+c_{pH}x_{Hf},\ c_{pH}=29\ \mathrm{J/(mole\ K)},$$

$$c_{pA}=(-8.101+0.1133T_f-7.206\times10^{-5}T_f^2+1.703\times10^{-8}T_f^3)\times4.19\ \mathrm{J/(mole\ K)}.$$

Heat conductivity of the gas phase is defined by empirical correlation for nonpolar binary mixtures [Reid et al., 1987]:

$$\lambda=q\lambda_{max}+(1-q)\lambda_{min},\ q=0.32(1-x_{Hf})+0.8x_{Hf},$$

$$\lambda_{max}=\lambda_A(1-x_{Hf})+\lambda_Hx_{Hf},\ \lambda_{min}=[(1-x_{Hf})/\lambda_A+x_{Hf}/\lambda_H]^{-1},$$

$$\lambda_A=0.01\left(\frac{T}{300}\right)^{1.75}\ \mathrm{W/(m\ K)},\ \lambda_H=0.183\left(\frac{T}{300}\right)^{0.75}\ \mathrm{W/(m\ K)}.$$

Intrinsic kinetic rate of benzene vapour hydrogenation on Pt/γ-Al_2O_3 [Ostrovskii et al., 1991] with the added reversibility correction factor:

$$W=\frac{kb_1P_AP_H^3}{1+b_1P_A+b_2P_AP_H^3+b_3\sqrt{P_H}}\left(1-\frac{K_eP_B}{P_AP_H^3}\right),$$

$$k=k_0\exp(-E/RT),\ k_0=3.6\times10^{-6}\ \mathrm{(mole\ A)/(m^3\ s\ Pa^3)},\ E=55\times10^3\ \mathrm{J/mole},$$

$$b_1=b_{10}\exp(Q_1/RT),\ b_{10}=1.5\times10^{-14}\ \mathrm{Pa^{-1}},\ Q_1=84\times10^3\ \mathrm{J/mole},$$

$$b_2=b_{20}\exp(Q_2/RT),\ b_{20}=10^{-30}\ \mathrm{Pa^{-4}},\ Q_2=92\times10^3\ \mathrm{J/mole},$$

$$b_3=b_{30}\exp(Q_3/RT),\ b_{30}=2.5\times10^{-16}\ \mathrm{Pa^{-1/2}},\ Q_3=113\times10^3\ \mathrm{J/mole},$$

$$K_e=K_{e0}\exp(-Q_r/RT),\ K_{e0}=2.3\times10^{35}\ \mathrm{Pa^3},\ Q_r=216\times10^3\ \mathrm{J/mole}.$$

The boundary value problem has been studied by means of the software package BPR-Q based on the continuation parameter method.

RESULTS AND DISCUSSION

Fig. 3 shows the calculated and experimental data on the temperature rise between the pellet center and gas flow on varying flow temperature for three gas flow compositions. We predicted critical phenomena on the catalyst pellet, which are associated with transitions between the kinetic and diffusion regimes. For benzene molar fraction 0.1, the calculated temperatures of ignition and extinction are almost equal (Figs. 3a and 4a). The calculated temperature rise inside the pellet, shown for comparison in Fig. 3, is significantly smaller than the interphase temperature difference in the maximum region. This corresponds to strong external diffusion limitation of the reaction rate in the middle flow temperature region. Additional confirmation was obtained by calculations of the molar fraction of benzene vapor (limiting transport reagent) at the pellet external surface (Fig. 4). If the flow temperature is 125 °C (Fig. 4a) we have a middle transition point between the internal and external regions. The fraction of benzene vapor on the pellet surface is slightly higher than a half of its flow value. This corresponds to the point of maximal flow-pellet temperature rise 95° in Fig. 3a. If the pellet temperature moves lower or higher than 210 °C (which corresponds to flow temperature 100 °C), the reaction shifts from the external to the internal diffusion region, which is accompanied by decrease in the apparent reaction rate. If pellet temperature becomes higher than 250 °C (flow temperature higher than 200 °C), a reverse reaction of cyclohexane dehydrogenation starts to make additional contribution to a decrease of ΔT. As a result, the pellet temperature rise disappears at flow temperature 350 °C and the catalyst comes to operate at the kinetic regime.

Similar results were obtained if molar benzene fractions in gas flow were 0.2 (Figs. 3b and 4b) and 0.3 (Fig. 3c and 4c). Experiments do not confirm model predictions concerning such critical phenomena as ignition and extinction of the catalyst pellet and corresponding hysteresis effect. However, there is a good agreement between the experimental and calculated values of flow-pellet temperature rise near the maximum and on the decreasing branch. In the point of maximum (Fig. 3a) the pellet temperature is about 210 °C. So, this value lies within the temperature interval 150<T<230 °C

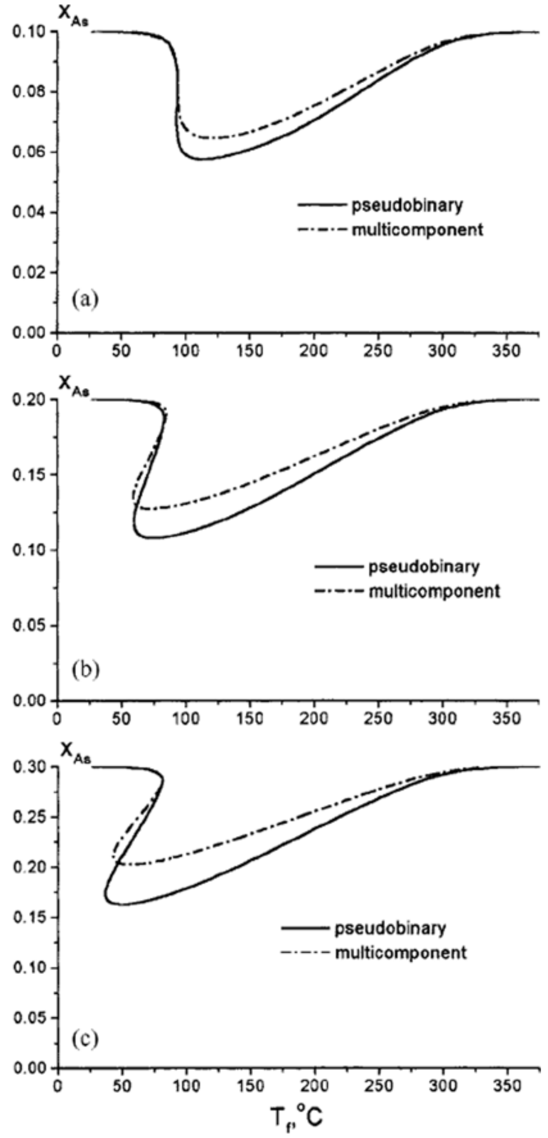

Fig. 4. Calculated benzene vapor fraction at pellet surface $x_{As}=x_A$ (R) dependence on gas flow temperature T_f for different benzene vapor molar fractions in gas flow mixture with H_2: x_{Af}=0.1 (a), x_{Af}=0.2 (b), x_{Af}=0.3 (c).

for which the kinetic rate expression (used in our model) was obtained by [Ostrovskii et al., 1991]. Lower stable kinetic branches at low flow temperatures are not observed in the experiments (Fig. 3). Possible explanation is that the real kinetic rate is underestimated by theoretical expression at such a low catalyst temperature.

Perhaps, the most important point is that the calculations performed by the multicomponent and pseudobinary mass transfer models give close results. The calculations appear to be sensitive to the parameters of interphase mass and heat transfer. By contrast, the calculations of internal mass transfer in macropores, made by the Dusty Gas and Maxwell-Stefan relations, practically coincide and are shown by unique solid curves in Figs. 3-6.

CONCLUSIONS

A simplified pseudobinary treatment of multicomponent internal mass transfer (in bimodal porous catalyst) and multicomponent external mass transfer (under forced convection) was derived from analytical estimations. To confirm the validity of the proposed treatment, we have compared the experimental data for benzene hydrogenation and rigorous calculations, based on the Dusty Gas and Maxwell-Stefan relations for internal transport and method of Stewart & Prober and Toor for interphase transport, and approximated (pseudobinary) calculations obtained by using the mathematical model of a spherically symmetric pellet. The simplified approach is quite accurate for the reactions A+nH=B of hydrogenation (n>0) and dehydrogenation (n<0) of sufficiently heavy compounds, i.e., if $D_{AH}\approx D_{BH}>>D_{AB}$. The results of numerical modeling and experimental verification show that benzene hydrogenation satisfies the above condition. Though, a priori analytical estimations were not so optimistic in quantitative sense.

For the considered class of reactions, the pseudobinary treatment (compared to the general multicomponent approach) has the following advantages: the ease of application even in the case of several reactions, compatibility with the Chilton-Colburn analogy and traditional empirical correlations for interphase transfer under forced convection, clear physical sense and quantitative criterion for validity. The results of this research may be of practical importance for solution of various problems concerning the effective and safe opera-

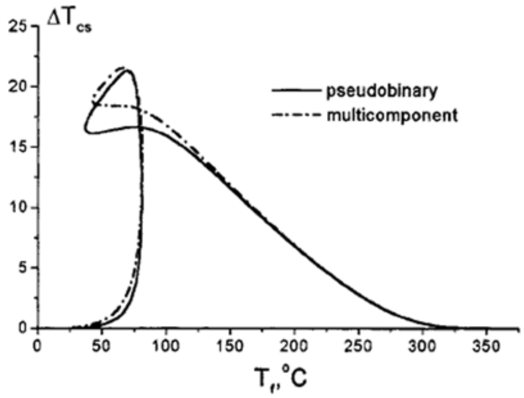

Fig. 5. Calculated intrapellet (surface-center) temperature rise ΔT_{cs} $=T(0)-T(R)$ dependence on gas flow temperature T_f. Benzene vapor molar fraction in gas flow mixture x_{Af}=0.3.

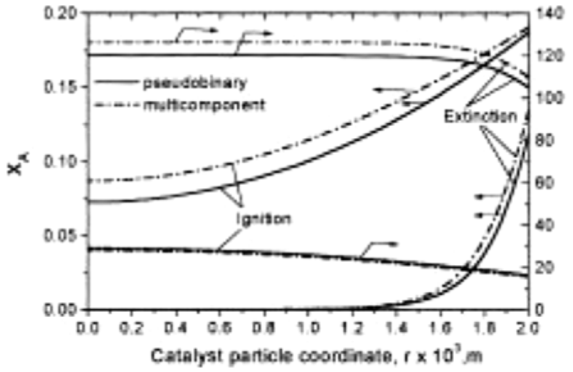

Fig. 6. Calculated profiles of flow-pellet temperature rise $T-T_f$ and benzene vapor molar fraction x_A along pellet radius r at the critical points of ignition and extinction in Fig. 3b. Benzene vapor molar fraction in gas flow mixture x_{Af}=0.2.

tion (prevention of hot spots and runaway) of the commercial trickle-bed (multiphase), multitube (gas phase) reactors and novel types of multifunctional structured catalytic reactors for hydrogenation or dehydrogenation of organic compounds.

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NOMENCLATURE

A : heavy reagent (benzene)
B : heavy product (cyclohexane)
C_t : gas mixture molar density [mole/m^3]
c_{pi}, c_p : molar heat capacity of gas components (i=A, B, H) and mixture [J/(mole K)]
D_{AB}, D_{AH}, D_{BH} : gas phase binary diffusion coefficients [m^2/s]
D_A, D_B, D_H : effective diffusion coefficient in multicomponent mixture [m^2/s]
D_p : coefficient of intrapellet diffusion [m^2/s]
D_* : coefficient of pseudobinary diffusion [m^2/s]
d_t : tube internal diameter [m]
E : activation energy [J/mole]
G : mass velocity of gas mixture [kg/(m^2 s)]
H : hydrogen
K_e : equilibrium constant for reverse reaction [Pa^3]
m_A, m_B, m_H : molar mass [kg/mole]
n : stoichiometric coefficient for hydrogen
N_A, N_B, N_H : molar fluxes [mole/(m^{2}s)]
P, P_A, P_H, P_B : total and partial pressure [Pa]
p_a : coefficient of macroporous permeability of pellet
p_i : coefficient of microporous permeability of macroglobules
Q_r : heat effect of reaction [J/mole]
Q_1, Q_2, Q_3 : specific heats of adsorption steps [J/mole]
R_g=8.31 : ideal gas constant [J/(mole K)]
R : catalyst pellet radius [m]
R_a : radius of macroglobules [μm]
r : coordinate along pellet radius or across diffusion film [m]
r_a : mean radius of macropores [A]
r_i : mean radius of micropores [A]
r_p : pore radius [A]
T : catalyst pellet temperature [C or K]
T_f : gas flow temperature [C or K]
V_H : hydrogen volume flow rate [m^3/s]
W : reaction rate [(mole A)/(m^3 s)]
x_A, x_B, x_H : molar fractions of A, B, H in gas mixture

Greek Letters

α : coefficient of gas-solid heat transfer [W/(m^{2}s)]
β : coefficient of gas-solid mass transfer [m/s]
ε_a : fraction of macropores in the pellet (macroporosity)
ε_i : fraction of micropores in macroglobules (microporosity)
ε_{ii} : fraction of micropores in the pellet
ε_{tot} : total porosity of the pellet
λ, λ_A, λ_H : coefficients of gas mixture and components heat conductivity [W/(m K)]
λ_p : coefficient of catalyst pellet heat conductivity [W/(m K)]
μ : coefficient of gas phase viscosity [(N s)/m^2]
ρ : gas mixture mass density [kg/m^3]

Dimensionless Criteria

Nu : Nusselt number
Pr : Prandtl number
Re : Reynolds number
Sc : Schmidt number
Sh : Sherwood number

Superscripts

K : Knudsen diffusion
M : molecular diffusion

Subscripts

a : macropores
A : heavy reagent (benzene)
B : heavy product (cyclohexane)
c : pellet center
f : gas flow
i : micropores
H : hydrogen
p : catalyst pellet
s : external surface of catalyst pellet

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