KINETICS OF CATALYTIC DEHYDRATION OF 1-PENTANOL

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Kinetic data of 1-pentanol dehydration on γ-alumina catalyst modified by potassium hydroxide were obtained using a continuous reactor with an internal recirculation. The conversion of 1-pentanol on this catalyst in the temperature range 300 – 390 °C and space velocity 1 – 8 kg $(h\ kg)^{-1}$ (molar fraction of water in the feed was in the range 0 – 0.56) was 50 – 98% and the selectivity with respect to 1-pentene was 50 – 84%. The following six reactions have been taken into account to describe the catalytic dehydration of 1-pentanol: direct formation of 1-pentene from 1-pentanol, formation of bis(1-pentyl) ether from 1-pentanol, disproportionation of the ether to 1-pentanol and 1-pentene, formation of 1-pentene from the ether, isomerization of 1-pentene to 2-pentene and hydrolysis of the ether to 1-pentanol. Treatment of experimental data by Langmuir–Hinshelwood models showed that the model involving adsorption of 1-pentanol accompanied by dissociation is the most suitable one.

1-Pentene is an important component in the production of copolymers[1] and intermediates for fine or specialty chemicals[2]. One possible way of preparation of 1-pentene is the catalytic dehydration of 1-pentanol. In the literature there are available data about dehydration of primary alcohols, mainly of ethanol and propanol[3,4]. For dehydration of primary alcohols, γ-alumina is often used as catalyst[5 – 7]. A modification of γ-alumina by alkaline metals increased the selectivity with respect to primary alkene formation. This is illustrated by the results of dehydration of 1-butanol poissoned by sodium hydroxide[5,6] or by the results of 1-pentanol dehydration on γ-alumina poissoned by potassium hydroxide[7]. Using tubular fixed bed reactor, 92% selectivity of the dehydration at 84% conversion of the alcohol were obtained on the last mentioned catalyst[7].

Mechanism of dehydration of primary alcohols includes several elementary steps. In order to describe catalytic dehydration of primary alcohols, the following summary chemical reactions are taken into account, where R–OH is primary alcohol, A1 is 1-alkene, E is ether and A2 is 2-alkene.

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$$\text{R-OH} \rightarrow \text{A1} + \text{H}_2\text{O} \tag{A}$$

$$2\,\text{R-OH} \leftrightarrow \text{E} + \text{H}_2\text{O} \tag{B}$$

$$\text{E} \rightarrow \text{A1} + \text{R-OH} \tag{C}$$

$$\text{A1} \rightarrow \text{A2} \tag{D}$$

$$\text{E} \rightarrow 2\,\text{A1} + \text{H}_2\text{O} \tag{E}$$

Krampera and Beránek[5,6] investigated catalytic dehydration of 1-butanol and found that reactions (*A*) and (*B*) proceed in comparable extent. The reaction paths of the ether to alkene transformation are still a matter of discussion. Knözinger and Köhne[3] studied dehydration of ethanol and preferred disproportionation of the ether (reaction (*C*)) as the more probable reaction since the less bonds are directly involved that in the formation of two olefin molecules with water elimination (reaction (*E*)). However, in real situations, both reactions (*C*) and (*E*) are parallel and seem to have some identical elementary steps.

In order to investigate chemical reaction kinetics, both differential and integral methods can be used. However, the differential methods based on initial rates evaluations are simpler and more valid to verify reaction mechanism[8,9] than the integral ones. On the other hand, due to very low conversions applied in the former methods, they are not very suitable for technological purposes. Kinetic models obtained from measurements at high conversions are preferred for the design of industrial chemical reactors. Kinetic experiments should be performed in such a way that both external and internal diffusion phenomena do not significantly influence the rate of process. Otherwise, the treatment of data is difficult. Berty's, Carbery's and other types of reactors with intensive internal mixing of media belong to the most common ones used for heterogeneous catalytic kinetic experiments[9]. The hydrodynamic regime in these reactors is near to ideal mixing and the following balance for each species can be written:

$$F y_{F,i} + W \sum_{j=1}^{n_r} \nu_{ji} \dot{\xi}_j - \Bigl(F + W \sum_{j=1}^{n_r} \dot{\xi}_j \sum_{i=1}^{n_c} \nu_{ji}\Bigr) y_i = 0 \tag{1}$$

$$i = 1, 2, \ldots, n_c$$

$$\dot{\xi}_j = \dot{\xi}_j \left(P, T, y_1, y_2, \ldots, y_{n_c}, k_{j1}, k_{j2}, \ldots, k_{jn_{rj}}\right) \qquad (2)$$

$$j = 1, 2, \ldots, n_r \, .$$

If the feed flow rate F, molar fractions in the feed $y_{F,i}$ and reaction conditions (P pressure, T temperature, k_{jk} kinetic parameters, $j = 1, \ldots, n_r$, $k = 1, \ldots n_{rj}$) are known, then one can obtain output mole fractions y_i by solving the system of non-linear algebraic equations (*1*) and (*2*). The Newton–Raphson method is very efficient to find the solution but a good initial judgment of y_i is needed that limits possibilities of usage minimization methods for kinetic parameter estimations. Only methods with small changes of parameter values during finding out minima are suitable. Due to small changes of parameters, the actual solution of Eqs (*1*) and (*2*) can be obtained from the initial judgment of variables equal to the solution from the preceding step. In our work we used the Nelder–Mead method[10].

EXPERIMENTAL

Chemicals. 1-Pentanol (99.6%), 1-pentene (99.7%) and bis(1-pentyl) ether (99.1%) were purified by distillation.

Catalyst. γ-Alumina (Cherox 3300, CHZ Litvínov) was in the form of hollow cylinders with the outer diameter 4.5 mm, the inner diameter 2.5 mm and the height 4.5 mm. The catalyst was impregnated with an aqueous solution of potassium hydroxide, then dried 20 h at the temperature of 80 °C and calcined at 400 °C for 3 h. The content of KOH in the dried catalyst was 0.05 wt.%. The surface area of the catalyst was 190 $m^2 g^{-1}$.

Apparatus and procedure. Experiments were carried out in a continuous reactor with inner recirculation and ca 15 cm^3 basket for the catalyst. Rotations of an impeller were checked by a magnetic induction device. Heating of the reactor was ensured by an electric cylinder furnance and temperature in the reactor was measured and controlled by regulator TRS 92 (accuracy ±0.5 °C). Reactants were fed into the reactor using pump MC 150 (accuracy ±2 rel.%). The reaction mixture was cooled in two condensators (10 °C and –50 °C) and the liquid mixture was collected in a vessel. Experiments were carried out under atmospheric pressure, the pressure in the reactor was measured by a pressure gauge (accuracy ±1.5 kPa). After reaching a steady state regime (after ca 6 h), the empty vessel was connected to the condenser and the reaction mixture was collected during one hour. Experiments were carried out with 12 g of the catalyst at the flow rate 12 – 96 g h^{-1} (space velocity 1 – 8 kg $(h\ kg)^{-1}$). Temperature in the reactor and the molar fraction of water in the feed varied within the range 308 – 385 °C and 0 – 0.56, respectively. Rotations of the impeller 1 400 min^{-1} together with the catalyst particle dimensions ensured that measurements were performed in the kinetic region.

Analysis. The liquid reaction mixture was analyzed using Hewlett–Packard 5890 gas chromatograph with dual flame ionization detectors. A glass column (inner diameter 3 mm) packed with 5% SE 30 on Chromaton NAW DMCS, 0.125 – 0.16 mm, was used. Analyses were performed in the temperature range 150 – 250 °C, with a temperature gradient of 10 °C min^{-1} and nitrogen as the carrier gas (flow rate 17 $cm^3 min^{-1}$). The following compounds were determined by gas chromatographic analysis: 1-pentanol, 1-pentene, bis(1-pentyl) ether and 2-pentene. The amount of water was calculated from a material balance. Molar fractions of the components in the gaseous reaction mixture were evaluated according to Dalton's law.

RESULTS AND DISCUSSION

Kinetic Experiments

In order to determine the extent of non-catalyzed reactions (*A*) – (*E*), some experiments without the catalyst were performed. We found that neither the dehydration of 1-pentanol nor the disproportionation of bis(1-pentyl) ether proceed to a significant extent. Under the experimental conditions comparable to the catalytic runs, the conversion of these reactants was less than 2 per cent.

The influence of the space velocity on the output composition, conversion and selectivity is evident from Figs 1 and 4. The expected trends, i. e. the increasing conversion with the decreasing space velocity and a maximum on the selectivity dependence, were confirmed. Experimental results obtained at different temperatures are summarized in Figs 2 and 5. The maximum selectivity 84% was achieved 613 K. Interesting results were obtained in the experiments with a mixture of 1-pentanol and water as a feed (Figs 3 and 6). As shown in Fig. 6, the selectivity is practically constant and does not depend on the molar fraction of water in the feed. This behaviour can be explained as follows: In the experiments with pure 1-pentanol, the conversion of 1-pentanol (about 85%) and the resulting molar fraction of water in the reaction mixture (0.45%) are rather high. If the feed into the reactor consists of 1-pentanol and water and dilution of the reactants is not very high (maximum molar fraction of water in the reaction mixture was 0.68), then a change of partial pressure of components does not cause significant changes of the reactions rates and the selectivity is approximately constant.

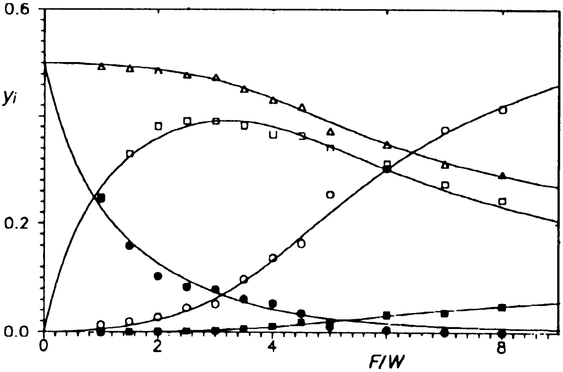

FIG. 1

Measured and calculated molar fractions (y_i) in output vs space velocity (*F*/*W*, kg (h kg)$^{-1}$). Temperature 623 K, feed: pure 1-pentanol. ○ 1-Pentanol, ☐ 1-pentene, ● 2-pentene, ■ bis(1-pentyl) ether, Δ water

Kinetic Models

In kinetic models, the following 5 chemical substances were considered: 1-pentanol, 1-pentene, water, bis(1-pentyl) ether and 2-pentene. A preliminary treatment of experimental data confirmed that chemical reactions (*A*) – (*E*) describe the investigated system sufficiently. Any other reactions or their reversibility, except reaction (*B*), need not to be taken into account. Several Langmuir–Hinshelwood (LH) models were used to express the reaction kinetics. Three of them gave the best fit of experimental values.

Model 1, proposed by Krampera and Beránek[5,6], suggest the surface reactions to be rate controlling steps and more than one kind of active centers exist on the catalyst surface. Model 2 differs from Model 1 by including an influence of the free active centers on the catalyst surface on the isomerization of 1-pentene.

Model 3 was derived under the following assumptions: (i) all active centers are equivalent for reactions (*A*) – (*E*), (ii) surface reactions are rate controlling steps, (iii) the adsorption of 1-pentanol is accompanied by its dissociation, (iv) two species at maximum (adsorbed component in molecular or dissociated form and vacant active center) can take part in chemical reaction. In spite of these assumptions, the LH equations could be regarded as some special empirical equations. Therefore, we extended the number of kinetic parameters including the exponent *e*. Furthermore, during parameter estimation, kinetic parameters close to zero were excluded.

Parameters of LH models were estimated by minimizing the objective function:

$$\omega = \sum_{k=1}^{n_c} \sum_{\substack{i=1 \\ i \neq 3}}^{n_m} w_{ki} \left(y_{ki}^{\text{exp}} - y_{ki}^{\text{calc}}\right)^2 , \qquad (3)$$

where

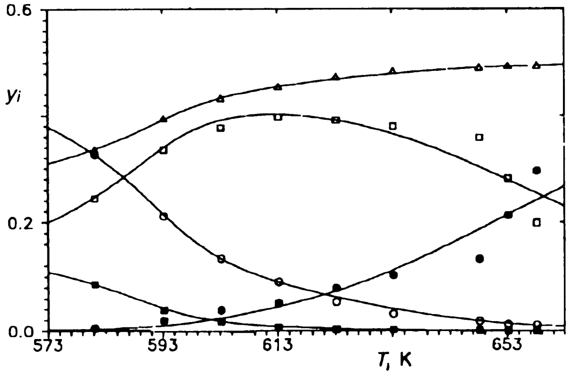

FIG. 2
Measured and calculated molar fractions (y_i) in output vs temperature T in the reactor. Space velocity 3 kg (h kg)$^{-1}$, feed: pure 1-pentanol. For designation see Fig. 1

$$w_{ki} = \begin{cases} 1/y_{ki}^{\exp}, & \text{if } y_{ki}^{\exp} \geq 0.1 ; \\ 10 & \text{if } y_{ki}^{\exp} < 0.1 . \end{cases}$$

Water (component 3) was not included into the objective function (Eq. (*3*)) because it was not directly determined in the reaction mixture. Values of y_{ki}^{calc} were obtained by the solution of Eqs (*1*) and (*2*). Parameters were estimated in three steps:

1. Estimation of kinetic parameters for constant temperature conditions (temperature T_{ref}, treatment of experimental data shown in Figs 1 and 2).
2. Estimation of temperature dependence of parameters (experimental data presented in Fig. 3).
3. Final treatment involving all the experimental data and the estimation of kinetic parameters as temperature dependent.

Temperature dependence of kinetic parameters was in the form:

$$k_{\text{T}} = k_{\text{T,ref}} \exp\left(- \frac{E\,(T_{\text{ref}} - T)}{R\,T\,T_{\text{ref}}}\right). \qquad (4)$$

An expression analogous to Eq. (*4*) was used for adsorption parameters but the sign in the exponential term was set to plus because, generally, the adsorption constants increase with decreasing temperature. In all the models used, the intermediate products of adsorption and kinetic constants were applied in the numerators of chemical rate expressions. This procedure gave better estimation of parameters but in some cases the negative values of "activation energy" appeared as the consequence of "summation" of activation energy and adsorption energy.

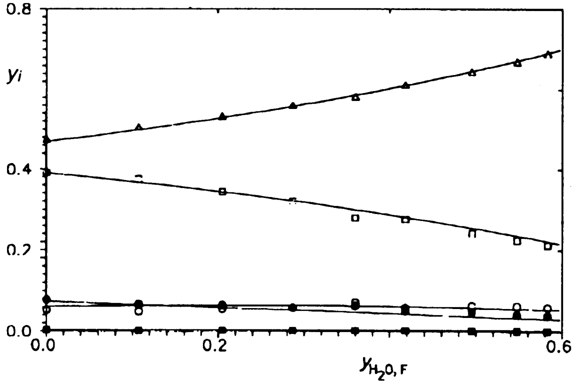

FIG. 3

Measured and calculated molar fractions (y_i) vs molar fraction of water in the feed ($y_{\text{H}_2\text{O,F}}$). Space velocity 3 kg (h kg)$^{-1}$, temperature in the reactor 623 K. For designation see Fig. 1

The first kinetic model (Model 1) tested was taken from papers of Krampera and Beránek[5,6]. This model is expressed by the following set of equations:

$$\dot{\xi}_1 = \frac{8\,k_1\,p_{\mathrm{pol}}}{(1 + \sqrt{1 + 8\,a_{\mathrm{pol}}})^3} \tag{5}$$

$$\dot{\xi}_2 = \frac{k_2\sqrt{p_{\mathrm{pol}}}}{1 + \sqrt{a_{\mathrm{pol}}}} - \frac{k_3\,p_{\mathrm{et}}\,p_{\mathrm{wat}}}{1 + a_{\mathrm{et}} + a_{\mathrm{wat}}} \tag{6}$$

$$\dot{\xi}_3 = \frac{k_4\,p_{\mathrm{et}}^2}{(1 + a_{\mathrm{et}})^2} \tag{7}$$

$$\dot{\xi}_4 = k_4\,p_{\mathrm{pen1}} \tag{8}$$

$$\dot{\xi}_5 = \frac{k_6\,p_{\mathrm{et}}}{(1 + \sqrt{2\,a_{\mathrm{et}}})^3}\,, \tag{9}$$

where

$$a_{\mathrm{pol}} = K_{\mathrm{pol}}\,p_{\mathrm{pol}}\,; \quad a_{\mathrm{pen1}} = K_{\mathrm{pen1}}\,p_{\mathrm{pen1}}\,;$$
$$a_{\mathrm{et}} = K_{\mathrm{et}}\,p_{\mathrm{et}}\,; \quad a_{\mathrm{wat}} = K_{\mathrm{wat}}\,p_{\mathrm{wat}}\,. \tag{10}$$

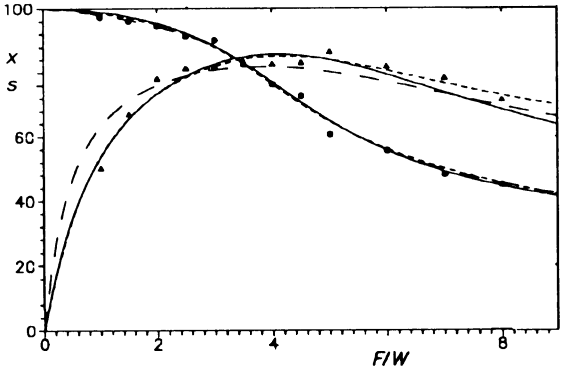

FIG. 4

Conversion of 1-pentanol (x, %) and selectivity of 1-pentene formation (s, %) vs space velocity (F/W, kg (h kg)$^{-1}$). Temperature in the reactor 623 K, feed: pure 1-pentanol. Parameters of models 1 –3 are in Table I. ● experimental conversion, ▲ experimental selectivity; Model 1, x and s designated by long broken line; Model 2, x and s designated by short broken line; Model 3, x and s designated by solid line

Parameters of Model 1 are summarized in Table I, along with the values of the objective function ω_1 computed with a weight of $w_{ki} = 1$, and the average difference for one measurement. All these quantities indicate that the better description of experimental data can be achieved by some other kinetic models. For that reason, we modified the expression for $\dot{\xi}_4$ as follows (Model 2):

$$\dot{\xi}_4 = \frac{k_5\, p_{\mathrm{pen1}}}{(1 + 2\sqrt{a_{\mathrm{pol}}} + a_{\mathrm{pen1}} + a_{\mathrm{wat}} + a_{\mathrm{et}})} \, . \qquad (11)$$

A decrease of both objective functions ω and ω_1 (Table I, Model 2), confirmed a success in modification of the Krampera–Beránek's model. Analysis of individual parameters in Models 1 and 2 indicates that the rate constants of bis(1-pentyl) ether disproportionation are equal to zero, which does not comport with literature data[3 – 7]. This discrepancy forced us to try other LH models. Both the number of parameters and the value of the objective function defined by Eq. (*3*) were considered in evaluating individual models. Equations (*12*) – (*16*) included in Model 3 with the parameters summarized in Table I fit experimental data very well.

$$\dot{\xi}_1 = \frac{k_1\, p_{\mathrm{pol}}^{e}}{D^2} \qquad (12)$$

$$\dot{\xi}_2 = \frac{k_2\, p_{\mathrm{pol}}^{2e} - k_3\, p_{\mathrm{et}}\, p_{\mathrm{wat}}}{D^2} \qquad (13)$$

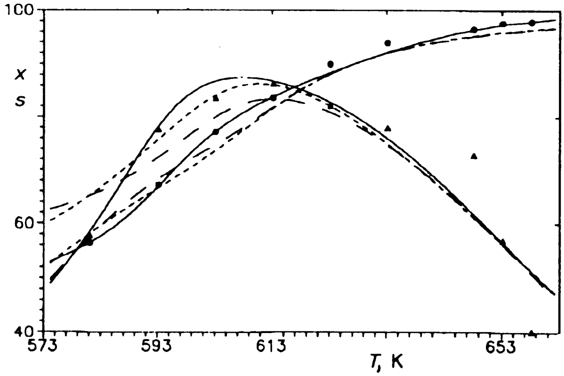

FIG. 5
Conversion of 1-pentanol (x, %) and selectivity of 1-pentene formation (s, %) vs temperature T in the reactor. Space velocity 3 kg (h kg)$^{-1}$, feed: pure 1-pentanol. Parameters of models are given in Table I. For designation see Fig. 4

$$\dot{\xi}_3 = \frac{k_4 \, p_{\mathrm{et}}}{D^2} \qquad (14)$$

$$\dot{\xi}_4 = \frac{k_5 \, p_{\mathrm{pen1}}}{D} \qquad (15)$$

TABLE I
Parameters of Langmuir–Hinshelwood models

Parameter	Model 1	Model 2	Model 3
k_1, mol (h kg kPa)$^{-1}$	13.4	10.3	48.6
E_{k1}, kJ mol^{-1}	65.7	65.0	67.4
k_2, mol (h kg^{-1}) kPa$^{-0.5}$	9.60	7.50	61.24
E_{k2}, kJ mol^{-1}	108	63.3	2.00
k_3, mol (h kg)$^{-1}$ kPa^{-2}	0.73	0.40	22.4
E_{k3}, kJ mol^{-1}	180.3	117.6	110.4
k_4, mol (h kg)$^{-1}$ kPa^{-2}	0.00	0.00	122.6
E_{k4}, kJ mol^{-1}	0.00	0.00	–3.70
k_5, mol (h kPa kg)$^{-1}$	0.10	0.25	0.37
E_{k5}, kJ mol^{-1}	156	123.30	107
k_6, mol (h kg)$^{-1}$ kPa^{-2}	0.00	50.8	130
E_{k6}, kJ mol^{-1}	0.00	54.3	69.30
K_{pol}, kPa^{-1}	0.05	0.051	0.246
E_{Kpol}, kJ mol^{-1}	1.46	1.18	0.01
$K_{\mathrm{pen1}} \cdot 10^3$, kPa^{-1}	0.13	0.13	0.13
E_{Kpen1}, kJ mol^{-1}	0.00	0.00	0.00
$K_{\mathrm{wat}} \cdot 10^3$, kPa^{-1}	0.13	0.13	13
E_{Kwat}, kJ mol^{-1}	0.00	0.00	55.4
K_{et}, kPa^{-1}	0.90	0.93	0.73
E_{Ket}, kJ mol^{-1}	0.17	0.10	19.02
e	–	–	0.59
ω	0.227	0.154	0.111
ω_1	0.040	0.027	0.020
δ	0.0105	0.0087	0.0067

$$\dot{\xi}_5 = \frac{k_6\, p_{\mathrm{et}}}{D^2} . \qquad (16)$$

In these equations, D is expressed as (*17*) and quantities a are defined by Eq. (*10*).

$$D = 1 + a^{e}_{\mathrm{pol}} + a_{\mathrm{pen1}} + a_{\mathrm{wat}} + a_{\mathrm{et}} . \qquad (17)$$

The computed profiles of molar fractions of the components in the reaction mixture predicted by Model 3 are drawn in Figs 1 – 3 as solid lines. As seen, a very good agreement between experimental and computed data is obtained. Similarly, Model 3 fits experimental data for the conversion and selectivity (Figs 3 – 6) better then Model 1 or Model 2.

The values of the parameters in Model 3 suggest the complicated paths of 1-pentanol dehydration. All five reactions (*A*) – (*E*) play a significant role in the investigated reaction system. It seems that the formation of 1-pentene via bis(1-pentyl) ether which is consequently consumed by reactions (*C*) and (*E*) proceeds predominantly. The value of parameter $e = 0.59$ is close to 0.5, which indicates that 1-pentanol is adsorbed with dissociation.

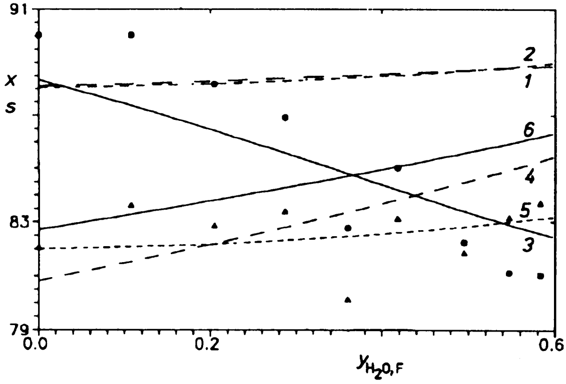

FIG. 6

Conversion of 1-pentanol (x, %) and selectivity of 1-pentene formation (s, %) vs molar fraction of water in the feed ($y_{H_2O,F}$). Space velocity 3 kg (h kg)$^{-1}$, temperature 623 K. *1* – *3* conversions of 1-pentanol predicted by Model 1, Model 2 and Model 3, respectively. *4* – *6* selectivities of 1-pentene formation predicted by Model 1, Model 2 and Model 3, respectively. ● Experimental conversion, ▲ experimental selectivity

SYMBOLS

a_i	activity of component i on the surface of catalyst
D	denominator in Langmuir–Hinshelwood model defined by Eq. (*17*)
e	exponent in the LH Model 3
E	activation energy, kJ mol^{-1}
F	feed flow rate, mol h^{-1}
k_i	kinetic parameter i, units see Table I

K	adsorption parameter, kPa^{-1}
$k_{T,ref}$	kinetic parameter valid for temperature T_{ref}
n_c	number of components
n_m	number of experiments
n_r	number of chemical reactions
n_{rj}	number of kinetic parameters of chemical reaction j
P	pressure, kPa
R	gas constant, 8.314 $J\ mol^{-1}\ K^{-1}$
s	selectivity of 1-pentene formation, %
T	temperature, K
w_{ki}	weight on component i in experimental point k
W	weight of catalyst, kg
x	conversion of 1-pentanol, %
y_{ki}	molar fraction of component i in output in experimental point k
δ	average difference between experimental and calculated molar fractions in output
ξ_j	rate of chemical reaction j
ν_{ji}	stoichiometric coefficient of component i in reaction j
ω	objective function defined by Eq. (3)
ω_1	sum of squared differences between experimental and calculated molar fractions of components in output

Subscripts

et	bis(1-pentyl) ether
pen1	1-pentene
pen2	2-pentene
pol	1-pentanol
wat	water

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