Heterogeneous catalytic reactions conditions optimization

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Abstract. Kinetic model of a heterogeneous catalytic reaction will be considered in this work and kinetic parameters will be determined. Based on the kinetic model, the problem of reaction conditions optimizations will be solved along with taking processes of reagents adsorption and desorption on solid catalyst into account.

Keywords: kinetic model, heterogeneous reaction, optimization of the conditions, adsorption on the surface of the catalyst.

1. Introduction

In the case of heterogeneous reactions, it is necessary to use more complex kinetic equations in the form of Langmuir-Hinshelwood relationships or regularities on the basis of the law of effective surfaces. Such equations are given in a scientific literature of development kinetic models, for example: reactions alkylation of benzene with ethylene [1-3] or dehydrogenation reaction of ethylbenzene [4].

Reaction of dehydrogenation ethanol to ethyl acetate is a reaction from sphere of "green chemistry", because bioethanol is used as raw material [5].

2. Kinetics of dehydrogenation ethanol to ethyl acetate

A detailed study of reaction kinetics dehydrogenation ethanol to ethyl acetate is given in [5]. The scheme of the reaction with main reversible stages is given (Table 1). The values of kinetic and adsorption parameters are determined.

Table 1. Scheme of chemical transformation and kinetic equations of reaction dehydrogenation ethanol to ethyl acetate.

Chemical reactions scheme	Kinetic equations
X1↔X2+X3	$w(1) = k(1) * \theta(1) - k(3) * \theta(2) * \theta(3)$
X1+X2↔X4+X3	$w(2) = k(2) * \theta(1) * \theta(2) - k(4) * \theta(4) * \theta(3)$

Where X1 – ethanol C_2H_5OH, X2 – acetaldehyde CH_3CHO, X3 – hydrogen H_2, X4 – ethyl acetate $CH_3COOC_2H_5$, $\theta(i)$ - catalyst surface fraction occupied by the i-th component (1), (2), i=1,…,4, $k(j)$ – rate constants of stages (dimension depends on the order stage), $w(1)$, $w(2)$ – reaction rates.

$$\theta^* = 1 - \sum_{i=1}^{4} \theta(i), \quad (1)$$

Where θ^* - free surface area of the catalyst at any time.

$$\theta(i) = \frac{b(i) * \frac{x(i)}{V}}{1 + \sum_{i=1}^{4} b(i) * \frac{x(i)}{V}}, \quad (2)$$

where *b(i)* - adsorption coefficient i-th substance, using the Langmuir-Hinshelwood mechanism for adsorbing reaction substances on a solid catalyst, *x(i)* - i-th substance concentration, [моль], V – volume of reaction mixture in a gas phase, [м^3], is determined based on a reactor geometric characteristics [5].

Values of activation parameters for rate constants and adsorption coefficients were determined in [5]. On a basis of developed kinetic model for a complex catalytic reaction, it is possible to optimize a reaction conditions [6, 7].

3. Optimization of conditions for catalytic heterogeneous reaction of dehydrogenation ethanol to ethyl acetate. Varying parameters and optimization objective functions

Studies of optimization catalytic reactions were initiated by G.K. Boreskov, M.G. Slinko, K. Denbig, Variable parameters for optimization problems in chemical kinetics are temperature, type of catalyst, catalyst concentration, pressure, etc. Experimental studies of the process under consideration were carried out at different values of temperature and pressure, which affects change in a volume of a reaction mixture. On this basis, as variable parameters, were considering temperature and pressure with corresponding physicochemical limitations presented in [5].

In general, optimization criterion based on a kinetic model has form [9-11]

$$R(\mathbf{x}, \mathbf{x^0}, t^*, \boldsymbol{\eta}, \mu, T, P) \to \max, \quad (3)$$

where x - vector of substance concentrations; x_0 - vector of initial substances concentrations; η – vector of substance weights; μ – additional expenses; t^* – reaction time, min; T – temperature, °C, P – pressure, atm.

4. Multicriteria optimization of conditions for catalytic heterogeneous reactions

Solution of a multicriteria optimization problem of conditions for carrying out the heterogeneous catalytic reaction ethanol dehydrogenation to ethyl acetate was carried out for optimization criteria: output of target product and output of by-product. Results of computational experiments are shown in Fig. 1-2. Thus, optimal conditions for carrying out a complex heterogeneous catalytic reaction using a multicriteria optimization method based on a kinetic model of a process are investigated.

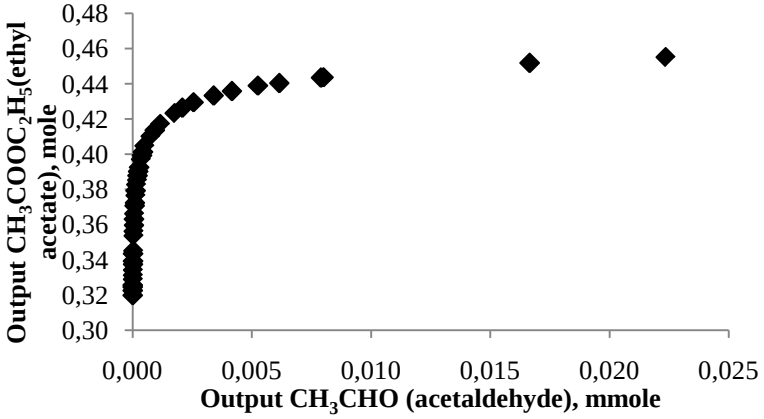

Figure 1. Approximations of Pareto front for reaction of dehydrogenation ethanol to ethyl acetate by NSGA-II algorithm.

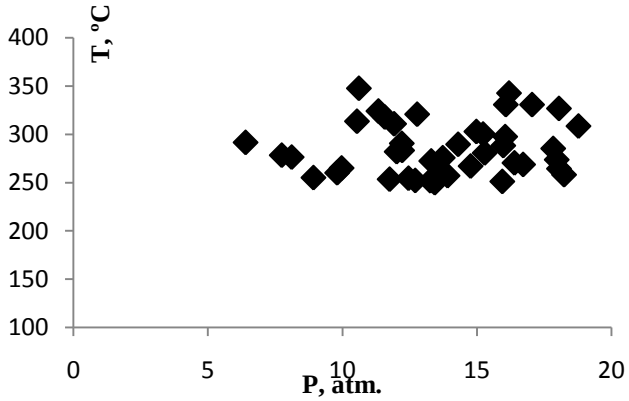

Figure 2. Approximations of Pareto set for reaction of dehydrogenation ethanol to ethyl acetate by NSGA-II algorithm.

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