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The cause and quantitative description of catalyst deactivation in the ethylene oxide hydration process

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Abstract

The ethylene oxide hydration process in a catalytic fixed-bed tube reactor was studied. A cross-linked styrene–divinylbenzene anion-exchange resin in the HCO_3^-/CO_3^{2-} form was used as a catalyst. The deactivation and swelling of the catalyst during the process was detected. The mathematical model of the reactor with determined parameters adequately describing the rate of the reaction, product distribution and catalyst deactivation and swelling has been developed.

Keywords: Catalyst deactivation; Modelling; Ethylene oxide; Hydration; Ethylene glycol

1. Introduction

Hydration of ethylene oxide is an industrial approach to glycols in general, and ethylene glycol in particular. Ethylene glycol is one of the major large-scale products of industrial organic synthesis, with the world annual production of about 15.3 million t/an in 2000 [1]. Hydration of ethylene oxide proceeds on a serial-to-parallel route with the formation of homologues of glycol:

$$H_2O \xrightarrow[k_0]{C_2H_4O} HOCH_2CH_2OH \xrightarrow[k_1]{C_2H_4O} HO(CH_2CH_2O)_2H \xrightarrow[k_2]{C_2H_4O} \text{etc.} \quad (1)$$

where k_0, k_1 and k_2 are the rate constants.

Now all ethylene and propylene glycol is produced in industry by a noncatalyzed reaction. Product distribution in reaction (1) is regulated by the oxide–water ratio in the initial reaction mixture. The ratio of the rate constants for the steps 2 to 1 of the reaction (1) is unfavorable for monoglycol formation. The distribution factor $b = k_1/k_0$ for a noncatalyzed reaction of ethylene oxide with water according to different data sources is in the range of 1.9–2.8 [2]. For this reason, large excess of water (up to 20 molar equiv.) is applied to increase the monoglycol yield on the industrial scale. This results in a considerable power cost at the final product isolation stage from dilute aqueous solutions.

One of the ways of increasing the monoglycol selectivity and, therefore, of decreasing water excess is the application of catalysts accelerating only the first step of the reaction (1). Typical examples of such catalysts would be the anions of salts of some acids [3–6,9] and metallate-anions [7,8]. The kinetics and reaction mechanism of α-oxide hydration using homogeneous catalysis by the salts (acetate, formate, oxalate, carbonate, bicarbonate, etc.) have been explicitly studied [3,10,11]. As evident from the kinetic data the distribution factor $b = k_1/k_0$ is reduced 10-fold (0.1–0.2) at the concentration of some salts of about 0.5 mol/l. This enables to produce monoglycol with high selectivity at water–oxide molar ratio close to 1.

Fig. 1 presents influence of (ethylene oxide)/(water) ratio on the ethylene glycol yield for noncatalytic, homogeneously and heterogeneously catalyzed reactions.

The properties of the above mentioned homogeneous nucleophilic catalysts were explored hereinafter in order to create the industrial heterogeneous catalysts of the selective hydration of ethylene oxide by means of an immobilization of anions of salts on heterogeneous carriers [12–17]. The largest ethylene glycol producers, such as Shell [18–24], Dow [25,26], BASF [27], Union Carbide [28–30] and Mitsubishi

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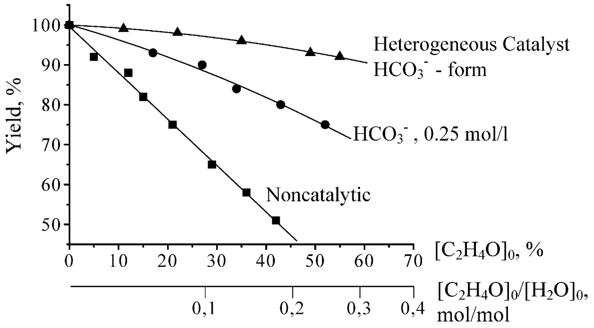

Fig. 1. Influence of (ethylene oxide)/(water) ratio on the ethylene glycol yield for noncatalytic, homogeneously and heterogeneously catalyzed reactions.

[31], conduct their studies on elaboration of selective catalysts of ethylene oxide hydration in the same direction.

In order to optimize the conditions for the catalyst exploitation it is necessary to have an adequate mathematical model of the heterogeneous catalytic process. The first step for creation of the model would be generation of a kinetic model of the homogeneous hydration of ethylene oxide, catalyzed by the bicarbonate anion in the concentrated water solutions. Such a model was prepared in our earlier report [32].

2. Experimental

2.1. Materials

$NaHCO_3$, ethylene glycol, diethylene glycol and triethylene glycol were purchased from commercial suppliers and used without further purification. Ethylene oxide was purified by distillation over solid NaOH. Water was purified by distillation.

Dow Chemical produced anion-exchange resins: DOWEX SBR, DOWEX MSA-1, DOWEX MARATHON A, activated by anion exchanging with sodium bicarbonate solution were used as catalysts. The properties of initial resins are summarized in Table 1.

2.2. Apparatus

All experiments were carried out in a tubular stainless laboratory reactor with the heat-exchanging jacket. Temperature in the reactor was maintained by circulating the thermostated silicone liquid through heat-exchanging jacket. Experiments were carried out at the constant temperature in the range of 95–115 °C and under pressure in a range of 1.5–2.0 MPa.

2.3. Analysis

Concentration of mono-, di- and tri-ethylene glycols in the reaction mixture was determined by GLC, using a $1\,\mathrm{m} \times 3 \times 10^{-3}\,\mathrm{m}$ glass column packed with 15% FFAP on INERTON AW-DMCS (0.2–2.25 mm). 2-Ethoxyethanol was used as an internal standard.

Ethylene oxide concentration was determined by treatment of the probe with HCl in dioxane followed by titration of the excess of HCl with NaOH [33].

Concentrations of carbonate and bicarbonate anions in the catalyst were determined by titration of solution obtained after full exchanging of carbonate and bicarbonate anions with chloride anion in 10% NaCl water solution.

3. Results and discussion

Series of experiments in the tubular reactor under a wide range of initial concentrations, temperatures, feed rates, and run time were carried out. During the experiments, composition of the outlet feed was determined, and activity and selectivity of the catalyst were estimated. As a measure of activity the effective first order rate constant was used

$$k_{\text{eff}} = \frac{\ln([C_2H_4O]_0/[C_2H_4O])}{t} \qquad (2)$$

The typical form of changing of activity and selectivity during run time is presented in Fig. 2.

3.1. Model of tubular plug-flow fixed-bed catalytic reactor

Development of the model was based on the following propositions:

- reaction volume consists of two phases: the liquid phase and the ionite (catalyst) phase;
- liquid phase streams through catalyst bed in a plug-flow regime;
- the catalytic and noncatalytic ethylene oxide hydration takes place in the ionite phase, and only noncatalytic reaction takes place in the liquid phase;
- the distribution of the components of the reaction mixture between liquid and ionite phases is a result of the rapid equilibrium;
- as it was shown experimentally, there are practically isothermic conditions inside the reactor.

Table 1
Properties of the anion-exchange resins

Resin	SBR	MSA-1	MARATHON A
Functional group	$-[PhN(CH_3)_3]^+$	$-[PhN(CH_3)_3]^+$	$-[PhN(CH_3)_3]^+$
Total exchange capacity (equiv./l)	1.4	1.0	17.2
Particle size (mm)	0.3–1.2	0.525–0.625	0.3–1.2
Matrix type	Gel	Macroporous	Gel

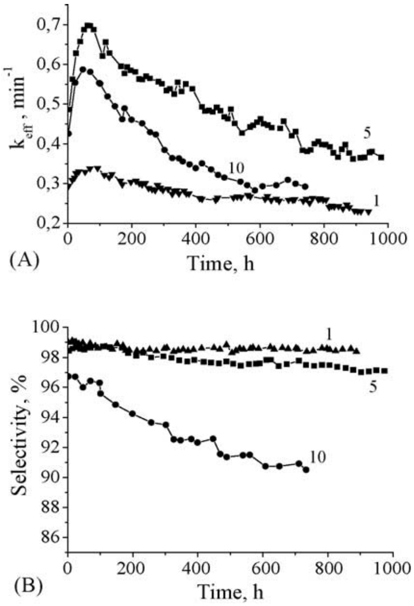

Fig. 2. (A) Changing of k_{eff} vs. time; (B) changing of selectivity vs. time. The numbers of curves corresponds to the numbers of experiments (Tables 2 and 3). Experimental conditions: 5, $[C_2H_4O]_0 = 12$ mass%, 105 °C, catalyst SBR; 10, $[C_2H_4O]_0 = 20$ mass%, 105 °C, catalyst SBR; 1, $[C_2H_4O]_0 = 12$ mass%, 95 °C, catalyst SBR.

Since the reactor is considered as a plug-flow reactor, changing of the molar flow (dF_j) and concentration (dC_j) of each component of reaction along with the reactor volume can be written as follows:

$$\begin{aligned} dF_j &= dV(\alpha r_{j\mathrm{i}} + (1-\alpha) r_{j\mathrm{l}}),\\ dC_j &= dt(\alpha r_{j\mathrm{i}} + (1-\alpha) r_{j\mathrm{l}}) \end{aligned} \qquad (3)$$

where $\alpha = V_{\mathrm{i}}/V$ is the ratio of ionite phase volume to reactor volume (ionite volume fraction), t the holding time, r the reaction rate, j the identification mark related to the component, i the identification mark related to the components of the ionite phase, and l the identification mark related to the components of the liquid phase.

The equations and rate constants, the same as for homogeneous reactions reported earlier we applied to the description of the reaction rates both in the ionite and the liquid phases [32]. For example, full kinetic equation for ethylene oxide consumption is as follows:

$$\begin{aligned} \frac{d[C_2H_4O]}{dt} &= (1-\alpha)\left(k_0[H_2O]_{\mathrm{l}} + 2.6k_0\left[\sum \mathrm{Gl}\right]_{\mathrm{l}}\right)\\ &\quad\times\left([H_2O]_{\mathrm{l}} + 1.84\left[\sum \mathrm{Gl}\right]_{\mathrm{l}}\right)[C_2H_4O]_{\mathrm{l}}\\ &\quad+\alpha\left(k_0[H_2O]_{\mathrm{i}} + 2.6k_0\left[\sum \mathrm{Gl}\right]_{\mathrm{i}}\right.\\ &\quad+k_{\mathrm{A1}}[HCO_3{}^-]_{\mathrm{i}} + k_{\mathrm{A2}}[CO_3{}^{2-}]_{\mathrm{i}}\\ &\quad+k_{\mathrm{HO^-}}[HO^-]_{\mathrm{i}} + 14k_{\mathrm{HO^-}}[HO^-]_{\mathrm{i}}\left[\sum \mathrm{Gl}\right]_{\mathrm{i}}/\\ &\quad\left.\times[H_2O]_{\mathrm{i}}\right)\left([H_2O]_{\mathrm{i}} + 1.84\left[\sum \mathrm{Gl}\right]_{\mathrm{i}}\right)\\ &\quad\times[C_2H_4O]_{\mathrm{i}} \end{aligned} \qquad (4)$$

where k_0 is the noncatalytic rate constant, k_{A1} the rate constant of bicarbonate-anion catalyzed reaction, k_{A2} the rate constant of carbonate-anion catalyzed reaction, $k_{\mathrm{HO^-}}$ the rate constant of hydroxyl-anion catalyzed reaction and $[\sum \mathrm{Gl}]$ the sum of all glycol's concentrations.

Concentrations of the components of the liquid phase have been determined by analysis of the outlet flow. Concentrations in the ionite phase were calculated from the following equilibrium equations:

$$\delta_1 = \frac{[SH]_{\mathrm{i}}[C_2H_4O]_{\mathrm{i}}}{[SH]_{\mathrm{l}}[C_2H_4O]_{\mathrm{l}}} \qquad (5)$$

$$\delta_2 = \frac{[H_2O]_{\mathrm{i}}}{[H_2O]_{\mathrm{l}}} \qquad (6)$$

$$\delta_3 = \frac{[\sum \mathrm{Gl}]_{\mathrm{i}}}{[\sum \mathrm{Gl}]_{\mathrm{l}}} \qquad (7)$$

The values of the equilibrium constants (δ_1, δ_2 and δ_3) were the only parameters determined from the experimental data using Eqs. (3) and (4). All other kinetic parameters were used from the kinetics acquired earlier [32]. All concentrations were determined experimentally including values of $[HCO_3{}^-]_{\mathrm{i}}$, $[CO_3{}^{2-}]_{\mathrm{i}}$ and $[HO^-]_{\mathrm{i}}$ measured at the starting and the ending points of the long-term experiments. The data in Table 2 show that the values of $\delta_1 \approx 1$ and $\delta_2 = \delta_3 = 0.5$ would allow to satisfactorily describe outlet concentrations.

So, system of equations (3) with experimentally determined parameters δ_1, δ_2 and δ_3 can serve as a mathematical model of the tube reactor for the steady state of the catalyst.

In reality, the catalyst changes its state during the run time due to two undesirable processes: deactivation (loss of active sites) and swelling. Loss of the catalytic activity causes decrease in selectivity (Fig. 2.). Rate of both the deactivation and the swelling directly correlates with the increase in the temperature, as well as ethylene oxide and glycol concentrations (Figs. 2 and 3 and Table 3).

In order to elaborate the model of the catalyst deactivation it is desirable to have the data of active site concentration during run time. The aforementioned steady state reactor model was used for calculation of the active site concentrations at each experimental time point using the acquired data of the outlet feed composition (dots in Fig. 3).

3.2. *Model of the catalyst deactivation and swelling*

Development of the model was based on the assumption that:

- active site loss occurs due to the following cleavage reactions:

$$-[N(CH_3)_3]^+ + OH^- \rightarrow -OH + N(CH_3)_3 \qquad (8)$$

Table 2
Comparison of the experimental and calculated by model (3) data of ethylene oxide conversion and ethylene glycol selectivity

Experiment number	Ionite	Experiment point	δ_1	Ethylene oxide conversion (%)		Ethylene glycol selectivity (%)	
				Experimental	Calculated	Experimental	Calculated
1	SBR	Start	0.81	95.6	95.6	98.1	98.3
		Finish	0.10	88.0	87.9	97.8	97.8
2	Marathon-A	Start	0.96	95.3	95.3	97.6	98.4
		Finish	1.28	88.5	88.5	98.0	97.2
3	MSA-1	Start	0.99	97.9	97.9	97.9	97.3
		Finish	0.99	86.0	86.0	97.7	97.8
4	MSA-1	Start	0.77	92.0	92.0	97.7	97.8
		Finish	0.79	83.6	83.7	95.8	95.8
5	SBR	Start	0.89	98.1	98.1	98.2	96.9
		Finish	1.09	85.9	85.9	97.1	95.5
6	MSA-1	Start	0.66	97.8	97.8	98.5	96.0
		Finish	0.88	77.5	77.5	97.8	95.3
7	MSA-1	Start	0.68	95.4	95.4	98.8	95.3
		Finish	1.21	82.3	82.3	92.9	92.2
8	SBR	Start	0.76	95.8	95.8	95.6	95.3
		Finish	0.97	80.1	80.1	95.2	91.2
9	SBR	Start	0.81	96.4	96.4	96.2	95.3
		Finish	0.92	78.2	78.2	95.0	90.4
10	SBR	Start	0.82	96.7	96.7	95.9	95.5
		Finish	0.94	81.4	81.4	90.5	91.4
11	SBR	Start	0.89	94.8	94.8	87.3	89.6
		Finish	0.95	80.6	80.6	76.4	76.1
12	SBR	Start	0.64	93.6	93.6	95.3	95.3
		Finish	0.53	82.5	82.5	91.5	91.2

$$-[\mathrm{N(CH_3)_3}]^+ + \mathrm{OH}^- \rightarrow -\mathrm{N(CH_3)_2} + \mathrm{CH_3OH} \qquad (9)$$

- catalyst swelling proceeds via ethylene oxide addition:

$$-\mathrm{N(CH_3)_2} + \mathrm{C_2H_4O} + \mathrm{H_2O} \rightarrow -[\mathrm{N(CH_3)_2C_2H_4OH}]^+\mathrm{OH}^- \qquad (10)$$

$$-[\mathrm{N(CH_3)_2C_2H_4OH}]^+ + n\mathrm{C_2H_4O} \xrightarrow{\mathrm{OH}^-} -[\mathrm{N(CH_3)_2(C_2H_4O)}_{n+1}\mathrm{H}]^+ \qquad (11)$$

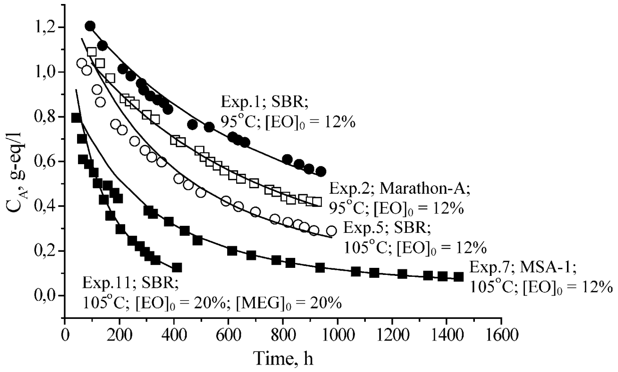

Fig. 3. Changing of active sites concentration vs. run time. Dots: calculated from experimental data by reactor model; lines: calculated by equation of deactivation (4).

$$-\mathrm{OH} + n\mathrm{C_2H_4O} \xrightarrow{\mathrm{OH}^-} -\mathrm{O(C_2H_4O)}_n\mathrm{H} \qquad (12)$$

- OH^- formation occurs due to hydrolysis of anions:

$$\mathrm{HCO_3}^- + \mathrm{H_2O} \rightleftarrows \mathrm{H_2CO_3(CO_2 + H_2O)} + \mathrm{OH}^- \qquad (13)$$

$$\mathrm{CO_3}^{2-} + \mathrm{H_2O} \rightleftarrows \mathrm{HCO_3}^- + \mathrm{OH}^- \qquad (14)$$

Having made the following assignments:

- active site concentration in ionite phase: $C_\mathrm{A} = [\mathrm{HCO_3}^-] + 2[\mathrm{CO_3}^{2-}]$;
- carbonate-anion fraction: $M = [\mathrm{CO_3}^{2-}]/([\mathrm{HCO_3}^-] + [\mathrm{CO_3}^{2-}])$;
- equilibrium concentration of OH^- anion: $[\mathrm{OH}^-] = K_\mathrm{h}[\mathrm{CO_3}^{2-}]/[\mathrm{HCO_3}^-] = K_\mathrm{h}M/(1-M)$, where K_h is the equilibrium constant of anion hydrolysis;
- rate of the active site cleavage can be described by the following equation with the first order concerning hydroxyl-anion and active sites concentrations:

$$\frac{\mathrm{d}N_\mathrm{A}}{V_\mathrm{cat}\,\mathrm{d}t} = k[\mathrm{OH}^-]C_\mathrm{A} = kK_\mathrm{h}\frac{M}{1-M}C_\mathrm{A} = k_\mathrm{d}\frac{M}{1-M}C_\mathrm{A} \qquad (15)$$

where N_A is the quantity of active site in the catalyst (mol) and k_d the deactivation rate constant.

Table 3
Catalyst swelling

Experiment number	Run time (h)	T (°C)	Initial concentrations (mass%)		Relative volume increase, $\Delta V/V_0$	
			Ethylene oxide	Ethylene glycol	Experimental	Calculated
1	939	95	12	0	0.53	0.74
2	925	95	12	0	0.56	0.76
3	713	95	12	0	0.38	0.52
4	533	95	12	0	0.4	0.68
5	978	105	12	0	1.24	1.47
6	667	105	12	0	1.29	1.08
7	1444	105	12	0	1.59	1.58
8	708	105	20	0	2.32	2.33
9	705	105	20	0	2.88	2.35
10	741	105	20	0	2.29	2.43
11	411	105	20	20	3.06	2.93
12	154	115	20	0	1.6	1.91

It was shown that the deactivation rate depends on ethylene oxide and glycol concentration, so the deactivation rate constant can be described by the following equation:

$$k_\mathrm{d} = \left[c + \frac{[\mathrm{C_2H_4O}]_0 + a[\mathrm{HOC_2H_4OH}]_0}{[\mathrm{H_2O}]_0 + [\mathrm{HOC_2H_4OH}]}\right] \exp\left(A - \frac{E}{RT}\right) \qquad (16)$$

A calculation of the active site loss (dots in Fig. 3) by Eqs. (15) and (16) gave the following values: $a = 1.50 \pm 0.24$, $c = 0.0727 \pm 0.0174$, $A = 21.10 \pm 0.98$, $E = 9677 \pm 384$ J/mol. With these parameters, Eqs. (15) and (16) provide ample description of the catalyst deactivation (lines in Fig. 3).

As catalyst mass increase proceeds due to ethylene oxide addition, the volume change can be expressed as follows:

$$V = V_0 + \frac{N_\mathrm{EO} M_\mathrm{EO}}{\rho} \qquad (17)$$

where V_0 is the initial catalyst volume, V the changed volume, N_EO the moles of ethylene oxide added, M_EO the mole weight of ethylene oxide and ρ the catalyst density.

Kinetic equation of ethylene oxide addition has the first orders concerning active sites and ethylene oxide concentrations:

$$\frac{\mathrm{d}N_\mathrm{EO}}{V\,\mathrm{d}t} = k_\mathrm{EO} C_\mathrm{A} [\mathrm{C_2H_4O}]_0 \qquad (18)$$

Mathematical transformation of the last equation gave the following expression:

$$\frac{\mathrm{d}[\mathrm{C_2H_4O}]}{\mathrm{d}t} = kC_\mathrm{A}\frac{M}{1-M} \times \left[c + \frac{[\mathrm{C_2H_4O}]_0 + a[\mathrm{HOC_2H_4OH}]_0}{[\mathrm{H_2O}]_0 + [\mathrm{HOC_2H_4OH}]}\right] \times [\mathrm{C_2H_4O}]_0 \qquad (19)$$

The best correspondence of calculated and experimental volumes (Table 3) has been achieved when parameters c and a are the same as in the equation of deactivation (16) and rate

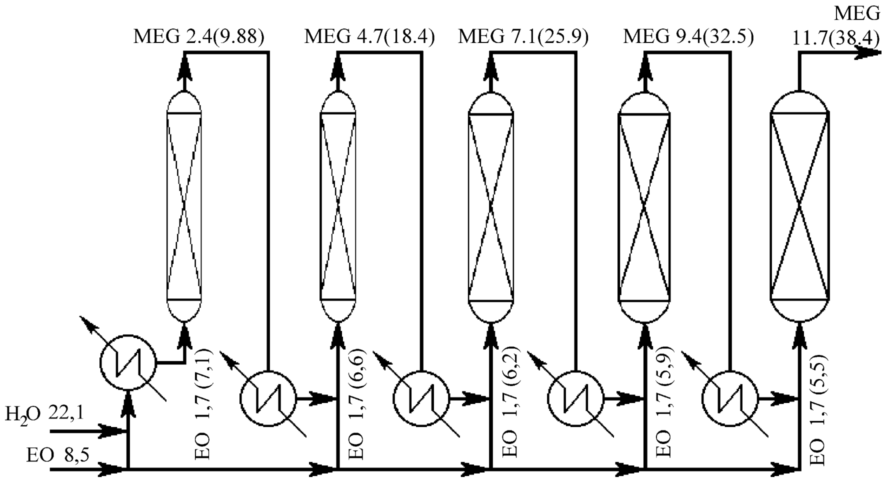

Fig. 4. Installation of ethylene glycol production, flow scheme. EO, ethylene oxide; MEG, monoethylene glycol; numerals: feeds (t/h); in parenthesis component concentration (mass%).

constant is expressed as

$$k\,(\mathrm{l/(mol\ min)}) = \exp\left((9.48 \pm 4.37) - \frac{(3852 \pm 1624)}{T}\right) \quad (20)$$

3.3. Modelling

A model of the catalytic reactor including kinetics of all the products formation (2, 3), deactivation (4, 5) and swelling (19) of the catalyst, was used for design and optimization of industrial tubular reactor of glycol production. Fig. 4 illustrates one of the possible schemes of industrial installation, which produces 11.7 t/h glycol on stream (38.4% glycol in outlet feed). This five-step reactor scheme can work up to 4000 h with 96–98.3% selectivity and catalyst swelling from 76.2 to 90.1 m^3. This technology allows us to save about 1.4 t of high pressure steam per 1 t of glycol at the water evaporation stage.

4. Conclusions

Catalytic hydration of ethylene oxide in the fixed-bed reactor with HCO_3^-/CO_3^{2-} form of anion-exchange resins has been described by the same kinetic equations with the same kinetic parameters as homogeneous catalytic reaction. The only distinction is a fast equilibrium distribution of reactants between liquid and ionite phases, which can be readily described by the corresponding equilibrium equations.

Kinetic model of the deactivation and swelling of the catalyst based on a series of chemical transformations of active sites of the catalyst has been developed.

All of the equations obtained can be used for design and optimization of different schemes of industrial catalytic reactors.

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