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INFLUENCE OF HYDROPEROXIDE EPOXIDATION REACTION CONDITIONS OF OCTEN-1 ON THE PROCESS OF Mo₂B ACTIVATION AND ON THE SELECTIVITY OF EPOXIDE FORMATION

<https://doi.org/10.23939/ctas2020.02.007>

A study of the process of activation of molybdenumboride catalyst in the reaction of epoxidation of octene-1 with tert-butyl hydroperoxide and the effect on this process of the initial concentration of octene-1, tert-butyl hydroperoxide and the amount of catalyst in the reaction mixture. As well as reaction products (tert-butyl alcohol and epoxy). It is shown that over time a new amorphous phase is formed on the surface of Mo₂B, which actually catalyzes the epoxidation reaction of octene-1 with tert-butyl hydroperoxide. The formation of this phase is the reason for the acceleration of the rate of consumption of hydroperoxide and the selectivity of the formation of epoxide over time.

Key words: oxidation, kinetic laws, catalyst, olefin.

Introduction

One of the important industrial reactions for the production of epoxy resins is the oxidation of unsaturated compounds in the presence of heterogeneous catalysts. It should be noted the high activity of molybdenumboride catalysts and especially when used as an oxidant – tert-butyl hydroperoxide. It was previously shown [1–4], that the time curves of hydroperoxide in the epoxidation of both octene-1 and β-ethylalyl-α-ethyl acrylate in the presence of a heterogeneous catalyst Mo₂B have an S-like character.

It is investigated that such dependence is connected with activation of the catalyst during reaction. If the process of epoxidation of octene-1, β-ethylalyl-α-ethyl acrylate, in the presence of inactivated forms of these catalysts, is studied in sufficient detail [1, 2, 5–7], while the stage of activation is practically not studied. Therefore, it was expedient to investigate the activation process in more detail, namely, the influence of the hydroperoxide epoxidation reaction conditions of octene-1 on the selectivity of epoxide formation in the presence of Mo₂B.

The aim of the study is to study the influence of the hydroperoxide epoxidation reaction conditions of octene-1 on the catalyst activation process and on the selectivity of epoxide formation in the presence of Mo₂B.

Materials and methods of research

The study was performed based on the process of hydroperoxide epoxidation of octene-1 in the presence of Mo₂B.

The following were used in the work: molybdenum boride of Mo₂B composition, brand “h” with a specific surface area of 220 m² / kg, determined by the method of nitrogen desorption.

Methods for obtaining and purifying other reagents, conducting experiments, analyzing the reaction mixture and processing kinetic curves are described in detail in [1–4].

Research results and their discussion

The activity of the Mo₂B catalyst in the epoxidation reaction of octene-1 with tert-butyl hydroperoxide increases over time and the flow curves of the hydroperoxide have a pronounced S-like character, which indicates the activation of the catalyst (Fig. 1).

Given that the reaction rate is influenced by two factors, the concentration of hydroperoxide and the activity of the catalyst, which change over time, the degree of activation of the catalyst (α) was calculated by the ratio (1):

$$\alpha = \frac{W_{\tau} / [\text{TBHP}]_{\tau} - W_0 / [\text{TBHP}]_0}{(W / [\text{TBHP}])_{\max} - W_0 / [\text{TBHP}]_0} \quad (1)$$

where $W_0 / [\text{TBHP}]_0$, $W_{\tau} / [\text{TBHP}]_{\tau}$, $(W / [\text{TBHP}])_{\max}$ – respectively, the given reaction rates are initial, running and maximum.

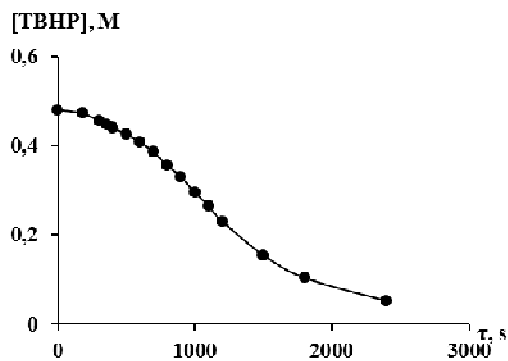


Fig. 1. Change in the concentration of tert-butyl hydroperoxide over time $[TBHP]_o = 0.48 M$, $[Oc]_o = 2.5 M$, $[Cat]_o = 0.22 m^2 / dm^3$, $T = 360 K$)

The degree of activation of the catalyst is influenced by both its amount (Fig. 2) and reactants (Fig. 3,4), and the reaction products – epoxide and tert-butanol (Fig. 5, 6).

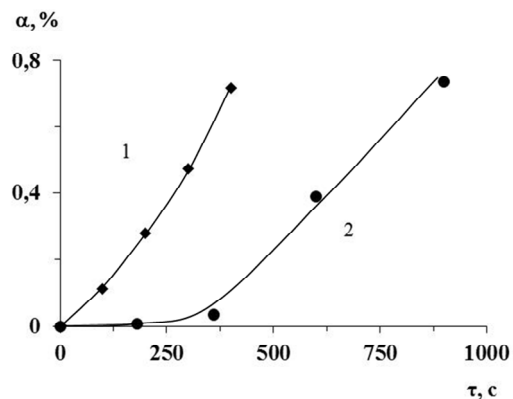


Fig. 2. Changing the degree of activation of the catalyst Mo_2B depending on its amount 1 – $[Cat]_o = 0.22 m^2 / dm^3$, 2 – $[Cat]_o = 0.1 m^2 / dm^3$, $[TBHP]_o = 0.5 M$, $[Oc]_o = 2.5 M$, $T = 360 K$)

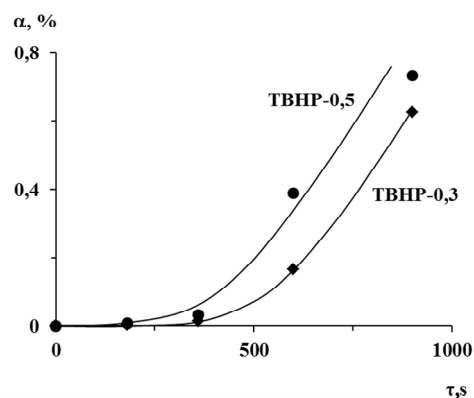


Fig. 3. Changing the degree of activation of the catalyst at different initial concentrations of tert-butyl hydroperoxide. ($[Oc]_o = 2.5 M$, $[Cat]_o = 0.22 m^2 / dm^3$, $T = 360 K$).

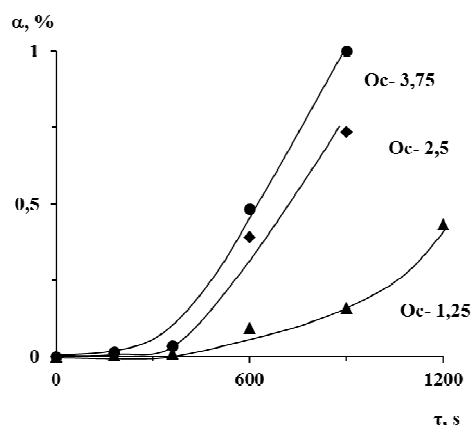


Fig. 4. Changing the degree of activation of the catalyst at different initial concentrations of octene-1. ($[TBHP]_o = 0.5 M$, $[Cat]_o = 0.22 m^2 / dm^3$, $T = 360 K$).

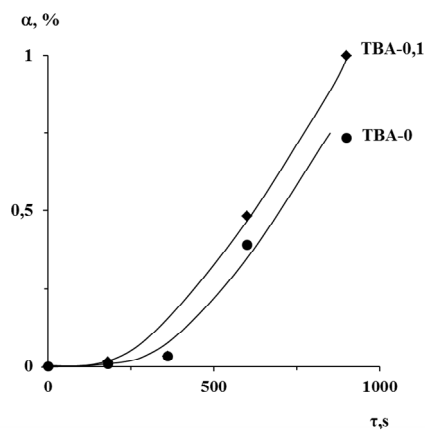


Fig. 5. Changing the degree of activation of the catalyst at different initial concentrations of tert-butyl alcohol introduced into the system. ($[TBHP]_o = 0.5 M$, $[Oc]_o = 2.5 M$, $[Cat]_o = 0.22 m^2 / dm^3$, $T = 360 K$).

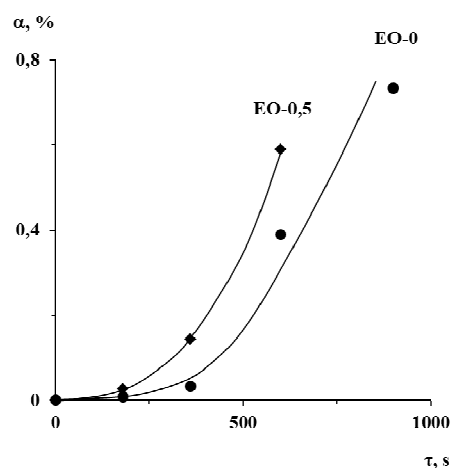


Fig. 6. Changing the degree of activation of the catalyst at different initial concentrations of epoxide introduced into the system. ($[TBHP]_o = 0.5 M$, $[Oc]_o = 2.5 M$, $[Cat]_o = 0.22 m^2 / dm^3$, $T = 360 K$).

The change in the degree of catalyst activation over time is described by the Avrami-Erofeev topochemical equation [8] (2).

$$\alpha = 1 - e^{-k_{\tau}\tau^n} \quad (2)$$

where τ is the reaction time, k_{τ} and n are the topochemical reaction constants.

This equation can be transformed into the form of a linear function:

$$\ln[-\ln(1-\alpha)] = \ln k_{\tau} + n \ln \tau \quad (3)$$

which allows to determine the topochemical constants k_{τ} and n by the graph-analytical method [9]. The function is really linear, but depending on the reaction conditions it can have one or two sections with different values of k_{τ} and n (Fig. 7).

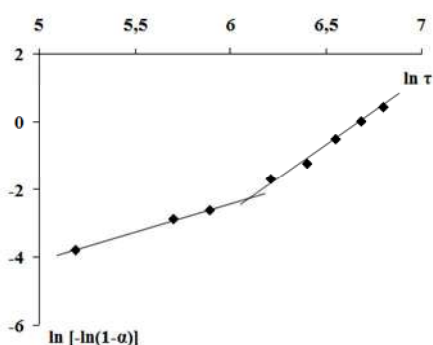


Fig. 7. Graphic solution of the Avrami-Erofeev equation

Table 1

The values of the topochemical constants k_{τ} and n depending on the reaction conditions are given below

$[\text{Oc}]_0 = 2,5 \text{ M}$, $[\text{Cat}]_0 = 0,22 \text{ M}^2/\text{DM}^3$, $T = 360 \text{ K}$

$[\text{TBHP}]_0, \text{M}$	n	k_{τ}	k_{ef}
0.5	$n_1 = 2.0416$	$k_{\tau 1} = 2.1 \cdot 10^{-7}$	$k_1 = 2.0 \cdot 10^{-4}$
	$n_2 = 4.0478$	$k_{\tau 2} = 1.8 \cdot 10^{-12}$	$k_2 = 12.5 \cdot 10^{-4}$

$[\text{TBHP}]_0 = 0.5 \text{ M}$; $[\text{Cat}]_0 = 0.22 \text{ M}^2/\text{DM}^3$; $T = 360 \text{ K}$

$[\text{Oc}] \text{ M}$	n	k_{τ}	k_{ef}
3.75	$n_1 = 2.229$	$k_{\tau 1} = 1.5 \cdot 10^{-7}$	$k_1 = 8.7 \cdot 10^{-4}$
	$n_2 = 4.1919$	$k_{\tau 2} = 1.5 \cdot 10^{-12}$	$k_2 = 15.1 \cdot 10^{-4}$
1.25	$n_1 = 1.0412$	$k_{\tau 1} = 1.8 \cdot 10^{-5}$	$k_1 = 2.8 \cdot 10^{-5}$
	$n_2 = 2.6262$	$k_{\tau 2} = 6.0 \cdot 10^{-9}$	$k_2 = 7.4 \cdot 10^{-4}$

$[\text{TBHP}]_0 = 0.5 \text{ M}$; $[\text{Oc}]_0 = 2.5 \text{ M}$.

$[\text{Cat}]_0 = 0.22 \text{ M}^2/\text{DM}^3$; $T = 360 \text{ K}$

$[\text{TBA}] \text{ M}$	n	k_{τ}	k_{ef}
0.1	$n = 3.3266$	$k_{\tau} = 2.8 \cdot 10^{-10}$	$k = 13.4 \cdot 10^{-4}$
0.3	$n = 4.2284$	$k_{\tau} = 7.7 \cdot 10^{-13}$	$k = 13.7 \cdot 10^{-4}$

The values of the effective reaction constants are related to the topochemical constant k_{τ} by the ratio (4):

$$k_{\text{ef}} = n \sqrt[n]{k_{\tau}} \quad (4)$$

The values of the effective constants for Mo_2B at the initial stage ($k_{1\text{ef}}$), respectively, is equal to $1.7 \cdot 10^{-4} \text{ s}^{-1}$, and at the stage of epoxidation ($k_{2\text{ef}}$), respectively, $13.0 \cdot 10^{-4} \text{ s}^{-1}$.

The selectivity of epoxy formation based on the reacted hydroperoxide increases over time (Fig. 8).

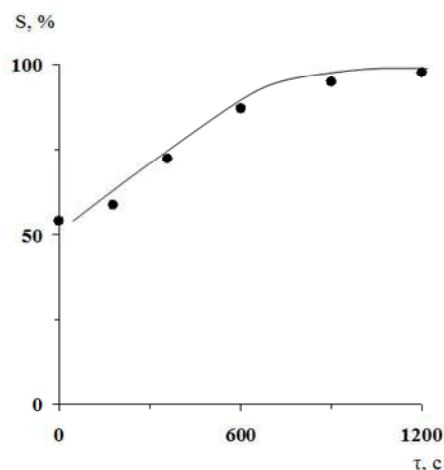


Fig. 8. Changing the selectivity of the formation of epoxy (S) over time

This effect is possible if the selectivity of epoxy formation on the inactivated catalyst is less than on the activated one.

The effective reaction rate constant on an inactivated catalyst is the sum of the effective reaction constants of unproductive decomposition hydroperoxide ($k_{1\text{ef}}(d)$) and epoxidation reactions ($k_{1\text{ef}}(e)$):

$$k_{1\text{ef}} = k_{1\text{ef}}(d) + k_{1\text{ef}}(e),$$

for Mo_2B $k_{1\text{ef}}(d) = 7.7 \cdot 10^{-5} \text{ s}^{-1}$ and $k_{1\text{ef}}(e) = 9.4 \cdot 10^{-5} \text{ s}^{-1}$.

This indicates that the epoxidation rate on the inactivated catalyst under these conditions is an order of magnitude lower than on the activated one.

On the inactivated form of the catalyst there is an unproductive consumption of hydroperoxide and the selectivity of the process should not exceed 55 %. With a change in the activity of the catalyst over time, the selectivity of epoxy formation, if the accepted model [10–13] is correct, should increase over time depending on

$$S = \frac{k_2^{\text{ef}} + (k_1^{\text{ef}}(e) - k_2^{\text{ef}}) e^{-k_{\tau}\tau^n}}{k_2^{\text{ef}} + (k_1^{\text{ef}} - k_2^{\text{ef}}) e^{-k_{\tau}\tau^n}} \quad (5)$$

where k_r and n are topochemical constants determined by the graphical solution of the Avrami-Erofeev equation. The calculated and experimental

values of selectivity coincide satisfactorily (Table 2), the above data indicate the adequacy of the adopted kinetic model of the reaction.

Table 2

Selectivity of formation of octene-1 epoxide in the presence of Mo₂B

Time, s	S calculated., %	S experimental., %
0	55.0	54.0
180	60.0	58.7
360	72.0	72.4
600	87.1	86.8
900	97.3	94.7
1200	100	97.4

Conclusions

The selectivity of epoxy formation depends on the degree of activation of molybdenum boride. The catalyst based on Mo₂B is characterized by a fairly high selectivity. However, the selectivity goes to zero $S \rightarrow 0$ if the degree of activation goes to zero $\alpha \rightarrow 0$.

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ВПЛИВ УМОВ РЕАКЦІЇ ГІДРОПЕРОКСИДНОГО ЕПОКСИДУВАННЯ ОКТЕНУ-1 НА ПРОЦЕС АКТИВУВАННЯ Mo₂B І НА СЕЛЕКТИВНІСТЬ УТВОРЕННЯ ЕПОКСИДУ

Проведено дослідження процесу активування молібденборидного каталізатора в реакції епоксидування октену-1 *трет*-бутилгідропероксидом і вплив на згаданий процес початкової концентрації октену-1, *трет*-бутилгідропероксиду і кількості каталізатора в реакційній суміші, а також продуктів реакції (*трет*-бутилового спирту і епоксиду). Показано, що в часі на поверхні Mo₂B утворюється нова аморфна фаза, яка власне каталізує реакцію епоксидування октену-1 *трет*-бутилгідропероксидом. Утворення цієї фази є причиною прискорення швидкості витрати гідропероксиду і селективності утворення епоксиду в часі.

Ключові слова: окиснення, кінетичні закономірності, каталізатор, олефін.