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ACTIVATION OF Mo_2B CATALYST IN THE EPOXIDATION REACTION OF α-ETHYLALLYL ETHYL ACRYLATE WITH *TERT*-BUTYL HYDROPEROXIDE

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Abstract. The regularities of Mo_2B catalyst activation in the epoxidation reaction of α-ethylallyl ethyl acrylate with *tert*-butyl hydroperoxide have been studied. It has been shown that the catalyst activation process is described by the Avrami-Erofeev topokinetic equation and includes two successive stages – the nucleation and formation of a new phase active in the epoxidation reaction. The formation of epoxy only occurs in the presence of the activated form of the catalyst. The effective and topochemical process constants have been calculated.

Keywords: oxidation, kinetic laws, catalyst, olefin.α

1. Introduction

The epoxidation reaction of unsaturated compounds is an important and promising reaction of organic chemistry. It allows transforming the double carbon-carbon bond into an epoxide ring and, in such a way, epoxides can be produced. Epoxides are important intermediates in industrial chemistry. They are widely used for the production of epoxy resins, epoxy composites, and bio-based epoxy thermosets.[1-9]

Moreover, epoxides are key materials for fine chemical synthesis due to their ring-opening activity.[10-18] Nowadays, the catalytic cycloaddition of CO_2 to different epoxides attracts considerable attentions of researcher all over the world as an efficient way for cyclic carbonates production as well as one of the best possible strategy for carbon dioxide neutralization by its fixation and recycling.[19-25]

Nevertheless, the direct epoxidation of unsaturated compounds with chemical oxidants, *e.g.*, organic hydroperoxides, leads to the formation of undesired by-products and is ineffective in many cases. The application of appropriate catalysts can solve the problem and improve the epoxide yield. Therefore, much attention has been focused on the application of different catalysts on the base of transition metal for the epoxidation process.[26-31] Among them, molybdenum compounds show much promise due to high catalytic activity.[32-35]

In particular, molybdenum boride catalysts are quite effective in the epoxidation reactions of olefins with *tert*-butyl hydroperoxide.[36-41] By using these catalysts, the rate of hydroperoxide consumption flow rate increases over time.[32,33,38,39,42] While in the case of Mo_2B_5 catalyst such an increase in the reaction rate is associated with partial dissolution of the catalyst and formation of an active homogeneous form of the catalyst in the reaction mixture,[42] in the case of Mo_2B, MoB, and MoB_2 catalysts it results from the catalyst surface activation.[33,38,40]

The process of the epoxidation of octene-1 and α-ethylallyl ethylacrylate in the presence of the activated forms of these catalysts has been studied in sufficient details.[32,33,38,39] However, the process of the activation of Mo_2B, MoB, and MoB_2 has been explored only for the epoxidation of octene-1.[43-45]

In this work, we studied the patterns of the activation of a Mo_2B catalyst in the oxidation reaction of α-ethylallyl ethylacrylate (EAEA) with *tert*-butyl hydroperoxide (TBHP) in toluene.

2. Experimental

The object of the study was the process of the hydroperoxide epoxidation of α-ethylallyl ethylacrylate in the presence of Mo_2B, accompanied by the catalyst activation.

α-Ethylallyl ethylacrylate (EAEA) was obtained by the Tishchenko reaction from α-ethyl acrolein in the presence of an aluminum isopropylate catalyst. The product purity was controlled chromatographically. *tert*-Butyl hydroperoxide (TBHP) was obtained by reacting hydrogen peroxide with *tert*-butyl alcohol in the presence of sulfuric acid. The freshly distilled hydroperoxide was used with the content of the main product over 99.5 %,

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and the TBHP purity was monitored by the iodometric titration. Toluene was used as an inert solvent. As a catalyst, a molybdenum boride (Mo_2B) powder, grade h, with the specific surface area of 0.220 m^2/g, determined by nitrogen desorption was used.

Epoxidation was performed in under argon blanket in a thermostated glass reactor equipped with a reflux condenser and a magnetic stirrer with a stirring speed of more than 900 rpm, which ensured the kinetic mode of the process.

The content of hydroperoxide in the reaction mass was determined by iodometric titration. Analysis of other components of the reaction mixture was performed by the method of individual reference substances on an LKhM-72 chromatograph with a thermal conductivity detector. To separate the components of the reaction mixture, a 3 m column with a diameter of 4 mm filled with 10 % apiezone L on N-AW chromaton was used with the column temperature of 450 K and carrier gas (helium) flow rate of 3.6 L/h.

Methods for obtaining and purifying other chemicals, conducting the experiments, analyzing the reaction mixture, and processing the kinetic curves are described in more detail elsewhere.[32,37,46]

3. Results and Discussion

As it has been shown,[46-50] the kinetic regularities of the epoxidation reaction of octene-1 and α-ethylallyl ethylacrylate differ from each other, both in the presence of the inactivated and activated forms of a Mo_2B catalyst. Thus, in the case of the epoxidation of octene-1, the reaction order for both the olefin and the hydroperoxide, both at the stage of catalyst activation and at the stage of epoxidation with activated catalyst, is equal to one. In the case of EAEA at the stage of catalyst activation, the reaction order for the olefin is 1, and, for the hydroperoxide, it is higher than one and close to 1.5; at the stage of epoxidation with the activated catalyst, the reaction order for the hydroperoxide is reduced to one, and for EAEA – to zero. Such differences in the general kinetic patterns in the epoxidation of octene-1 and EAEA are due to the different ability to form intermediate complexes of these olefins, both with the activated and inactivated catalyst, namely, a greater affinity of EAEA to the catalyst compared to octene-1. The increase in the activity of the catalyst over time is evidenced by the extreme course of the function $w_\tau = \varphi(\tau)$ (Fig. 1). As it is seen from the data in Fig. 1, the flow rate of the hydroperoxide (w_τ) increases with time to a certain maximum value (w_{max}), after which it decreases naturally. Similarly, the rate of epoxy formation (w_τ^e) changes over time (Fig. 1). However, the function $w_\tau^e = \varphi(\tau)$, in contrast to the function $w_\tau = \varphi(\tau)$, comes from almost zero.

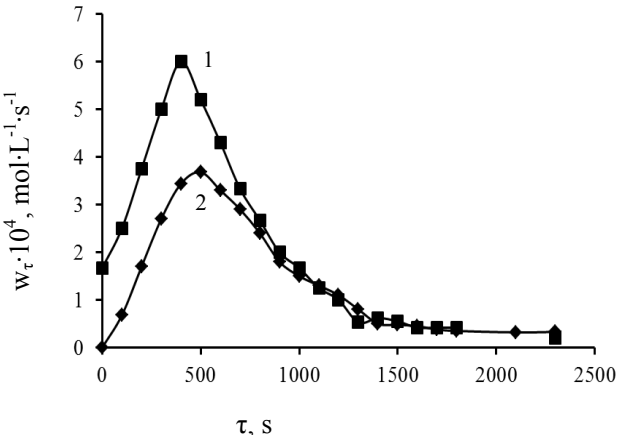

Fig. 1. Time variation of the *tert*-butyl hydroperoxide consumption rate (w_τ) (1) and change in the rate of epoxy accumulation w_τ^e over time (2). [TBHP]o = 0.5 mol/L, [EAEA]o = 2.2 mol/L, [Cat]o = 0.3 m^2/L, T = 383 K

This indicates that, on the inactivated catalyst (Kt^n), the epoxide is practically not formed and the hydroperoxide is mainly spent on the activation of the catalyst. With the appearance of the activated form of the catalyst (Kt^*) begins, in fact, the epoxidation reaction with its participation. The time intervals needed to reach the maximum flow rate of the hydroperoxide $(w_\tau)_{max}$ and the maximum rate of epoxy formation $(w_\tau^e)_{max}$ are close. After the point of a maximum speed, the flow rate of hydroperoxide and the rate of epoxy formation are almost equalized.

If the epoxide is formed with the participation of both the inactivated ($[Kt^n]$) and activated ($[Kt^*]$) catalyst, then given the first order of the reaction for the hydroperoxide, the total rate of epoxy formation over time w_τ^e should be described by the equation:

$$w_\tau^e = k_{ef(e)}^n [TBHP][Kt^n] + k_{ef(e)}^a [TBHP][Kt^*] \quad (1)$$

where $k_{ef(e)}^n$ and $k_{ef(e)}^a$ are effective rate constants for the formation of the epoxide with the participation of the inactivated and activated catalyst, respectively.

The conversion degree of the inactivated catalyst to the activated one (α), the content of the initial amount of the catalyst ($[Kt]_0$), and the amounts of its inactivated ($[Kt^n]$) and activated ($[Kt^*]$) forms are related by the relations:

$$[Kt^*] = [Kt]_0 \cdot \alpha \quad \text{and} \quad [Kt^n] = [Kt]_0 \cdot (1-\alpha) \quad (2)$$

If in the region of the maximum reaction rate, the degree of catalyst activation is close to one, and the initial rate of epoxy formation is close to zero, the change in the degree of catalyst activation with time can be estimated from the ratio:

$$\alpha_\tau = \left(\frac{w_\tau^e}{[\text{TBHP}]}\right)_\tau : \left(\frac{w_\tau^e}{[\text{TBHP}]_\tau}\right)_{\max} \quad (3)$$

where $\left(\frac{w_\tau^e}{[\text{TBHP}]}\right)_\tau$ and $\left(\frac{w_\tau^e}{[\text{TBHP}]_\tau}\right)_{\max}$ are running and maximum reduced epoxy formation rates, respectively. The above rate of the epoxy formation will be related to the degree of the activation of the catalyst by a linear dependence:

$$\frac{w_\tau^e}{[\text{TBHP}]_\tau} = k_{ef(e)}^n + (k_{ef(e)}^a - k_{ef(e)}^n)\alpha \quad (4)$$

The data in Fig. 2 show that the actual rate of the epoxy formation increases linearly as the degree of catalyst activation increases, but the line of this function comes from the origin, which confirms the conclusion about the epoxidation reaction only with the activated form of the catalyst.

The value of the effective rate constant of the epoxy formation reaction under the reaction conditions is defined as the tangent of the angle of inclination of the direct function

$$\left(\frac{w_\tau^e}{[\text{TBHP}]}\right)_\tau = \varphi(\alpha), \quad \text{equals} \quad k_{ef(e)}^a = 13.59 \cdot 10^{-4} \text{ s.}$$

The function $\alpha = f(t)$ has an s-shaped form (Fig. 3), characteristic of topochemical processes. For their quantitative description, the Avrami-Erofeev equation was used:[51-53]

$$\alpha = 1 - e^{-k_t t^n} \quad (5)$$

where k_t and n are the topochemical process constants.

The values of the topochemical constants k_t and n have been determined by the graph-analytical method based on the linear dependence:

$$ln(-ln(1-\alpha)) = ln\, k_t + nlnt\,, \quad (6)$$

which should be observed if the process of the catalyst activation can be described by dependence (5).

Fig. 4 shows that there are two linear regions that describe the activation process and are characterized by different values of topochemical constants. If in the first section the value of the topochemical constant $n_1 < 2$ and, accordingly, $n_1 = 1.62$, and $k_{t1} = 5.83 \cdot 10^{-5}$ then in the second section $n_2 > 2$, it is equal to 2.6, and $k_{t2} = 2.42 \cdot 10^{-7}$.

It should be noted that the main process of the catalyst activation occurs probably in the second section and is characterized by the topochemical constants n_2 and k_{t2}. This is evidenced by both the values of the catalyst activation degree, which in the first section does not exceed 30 % and by the low conversion of the hydroperoxide (~23 %) and the selectivity of the epoxy formation (~8 %).

Probably, the first section is mainly responsible for the nucleation stage and, under the experimental conditions of this, it lasts ~270 s. In the second section, the catalyst activation degree varies in the range of 0.3-0.95; the hydroperoxide conversion falls in the range of 20-95 % and the selectivity of epoxy formation 10-95 %. Probably, in this period the formation of a new, more active form of the catalyst takes place.

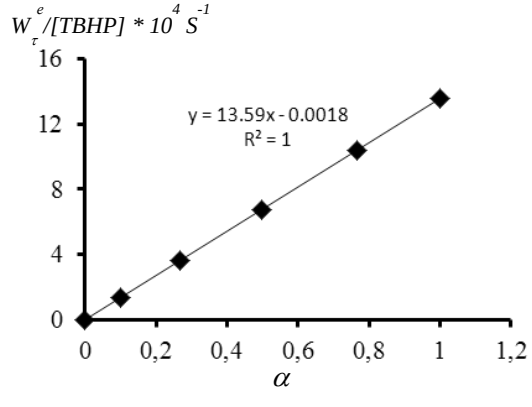

Fig. 2. Dependence of $\frac{w_{\tau e}}{[\text{TBHP}]_\tau}$ on the degree of activation of the Mo_2B catalyst. $[TBHP]_o = 0.5$ mol/L, $[EAEA]_o = 2.2$ mol/L, $[Cat]_o = 0.3$ m^2/L, $T = 383$ K

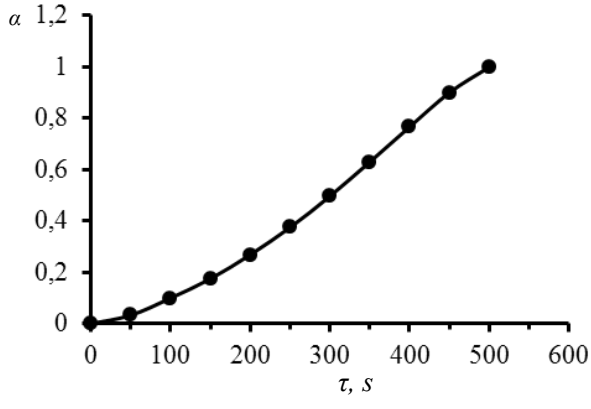

Fig. 3. Time variation of the degree of activation of the Mo_2B catalyst. $[TBHP]_o = 0.5$ mol/L, $[EAEA]_o = 2.2$ mol/L, $[Cat]_o = 0.3$ m^2/L, $T = 383$ K

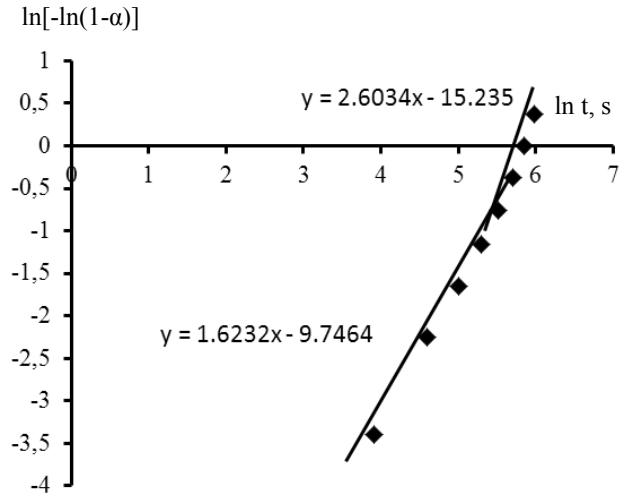

Fig. 4. Graphical solution of the Avraami-Erofeev equation: $[TBHP]_o$ = 0.5 mol/L, $[EAEA]_o$ = 2.2 mol/L, $[Cat]_o$ = 0.3 m^2/L, T = 383 K

4. Conclusions

The process of the activation of the Mo_2B catalyst is associated with the modification of its surface under the action of the reaction medium. This process includes at least two main stages - the nucleation stage and the stage of the formation of the more active and selective phase of the catalyst, which is a subject to the patterns of topochemical reactions and is described by the Avrami-Erofeev topochemical equation. The selectivity of the epoxide formation on the inactivated catalyst is close to zero. The selectivity of the epoxide formation on the activated catalyst is quite high and falls into the range of 95-98 %.

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АКТИВУВАННЯ КАТАЛІЗАТОРА Mo_2B В РЕАКЦІЇ ЕПОКСИДУВАННЯ α-ЕТИЛАЛІЛЕТИЛАКРИЛАТУ *трет*-БУТИЛГІДРОПЕРОКСИДОМ

Анотація. *Вивчено закономірності активування каталізатора Mo_2B у реакції епоксидування α-етилалілетилакрилату трет-бутилгідропероксидом. Показано, що процес активування каталізатора описується топохімічним рівнянням Аврамі-Єрофеєва і мыстить дві послідовні стадії – зародкоутворення і формування нової фази, активної в реакції епоксидування. Утворення епоксиду відбувається тільки в присутності активованої форми каталізатора. Обчислено ефективні й топохімічні константи процесу.*

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