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ACTIVITY OF VANADIUM COMPOUNDS IN REACTION OF EPOXIDATION OF 1-OCTENE AND DECOMPOSITION OF *TERT*-BUTYL HYDROPEROXIDE

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The influence of vanadium-containing compounds as catalysts on the reaction of 1-octene epoxidation by *tert*-butyl hydroperoxide and the decomposition of this hydroperoxide was investigated. It is shown that the catalytic activity of vanadium compounds depends on catalyst ligand nature. It is established that vanadium boride and carbide are the most active catalysts for hydroperoxide epoxidation, while V_2O_5 is the most active catalyst of *tert*-butyl hydroperoxide decomposition. The highest selectivity of 1,2-epoxyoctene formation is observed when VC is used as a catalyst.

Keywords: epoxidation, catalysts, vanadium compounds, 1-octene, *tert*-butyl hydroperoxide.

Introduction

The epoxidation is a valuable reaction of organic synthesis for production of epoxies of unsaturated compounds as well as an important industrial reaction for production of epoxy resins. Moreover epoxy compounds can serve for further transformations [1–3]. All components of the reaction mixture have a significant effect on the proceeding of the hydroperoxide epoxidation reaction of olefins, including nature of oxidant, unsaturated compound, solvent, reaction products, and firstly catalyst nature.

Heterogeneous catalysts are the most attractive catalysts for hydroperoxide epoxidation reactions because of their technological advantages in application; among them transition metal heterogeneous catalysts show much promise due to ability to exhibit a variable oxidation state [4–6]. Great attention in literature is focused on various vanadium containing compounds with varied ligands and supports as well as their catalytic ability investigation. Thus, epoxidation of cycloolefins, cyclooctene and cyclohexene, were successfully realized with application as catalysts *bis*-acetylacetonato-oxo vanadium complex supported on nano- γ -AlO(OH) [7] and vanadia supported on chromium-containing acid-activated bentonite [8], in the case of allylic alcohols – vanadium supported on sulfated titanium pillared montmorillonite [9] and immobilized polymer-

supported vanadium-binaphthylbishydroxamic acid complex (PS-VBHA) [10], the case of propene – copper modified by vanadium ($VO_x \cdot Cu$) [11] and K/V/SiO₂ [12].

Aim of the work

The purpose of the work is to investigate the influence of ligand nature on catalytic activity of vanadium compounds in the epoxidation reaction of 1-octene by *tert*-butyl hydroperoxide and the reaction of *tert*-butyl hydroperoxide decomposition.

Materials and methods

For investigations were used:

- 1-octene (OK), was obtained from Aldrich, was additionally distilled before use, 98 %;
- chlorobenzene, reagent chemically pure grade, was additionally dried and distilled before use, 98 %;
- *tert*-butyl hydroperoxide (TBHP) was synthesized by the procedure in [13], 99,5 %;
- 1,2-epoxyoctane (EPO), was obtained from Aldrich, 98 %;
- vanadium-containing compounds, exactly, VB₂, VC, VSi₂, V₂O₅, were commercial chemicals of chemically pure grade of Donetsk factory of chemical reagents. BET surface area of V-compounds were determined by low temperature nitrogen adsorption-desorption method using ASAP 2010 and were equal (m²/g): VB₂ – 1,2; VC – 1,5; VSi₂ – 1,8; V₂O₅. – 1,9.

The catalytic activity of vanadium-containing compounds was investigated in thermostated glass reactor fitted with areflux condenser in solution of chlorbenzene. Continuous agitation was carried out using the magnetic stirrer. In a typical run, reagents, 1-octene, *tert*-butyl hydroperoxide and chlorbenzene or *tert*-butyl hydroperoxide and chlorbenzene were loaded into the reactor. The reaction mixture was heated up to 95 °C by circulation of heated carrier through reactor shell and only after that catalyst was added. The introduction of the catalyst was considered as the start of the reaction. Initial concentration of 1-octene and *tert*-butyl hydroperoxide were equal $[OK]_0 = 3 \text{ mol/l}$ and $[TBHP]_0 = 0,5 \text{ mol/l}$, respectively. Catalyst content in the reaction system was equal $9 \text{ m}^2/\text{l}$. During the course of the reaction, samples of reaction mixture were withdrawn periodically for analysis.

Tert-butyl hydroperoxide concentration was determined by iodometric titration. The reaction products were analyzed by chromatographic method.

Conversion of *tert*-butyl hydroperoxide (K), selectivity of 1,2-epoxycyclooctane formation (S) and yield of 1,2-epoxycyclooctane (Y) were calculated as:

$$K = \frac{[TBHP]_0 - [TBHP]}{[TBHP]_0}$$

$$S = \frac{[EPO]}{[TBHP]_0 - [TBHP]} \cdot 100\%$$

$$Y = \frac{[EPO]}{[TBHP]_0} \cdot 100\%$$

where $[TBHP]_0$ – initial concentration of *tert*-butyl hydroperoxide; $[TBHP]$ and $[EPO]$ – concentration of *tert*-butyl hydroperoxide and 1,2-epoxycyclooctane in definite moment of time, respectively.

Results and discussion

It is necessary to note that in the absence of vanadium compounds in the reaction system, as it was established by additional experiments, *tert*-butyl hydroperoxide is practically not consumed (hydroperoxide conversion was 4 for 60 min) and reaction product, 1,2-epoxyoctane is not formed under the hydroperoxide epoxidation reaction conditions. The non-catalytic epoxidation process of 1-octene by *tert*-butyl hydroperoxide does not proceed under the investigated conditions. In the presence of V-compounds both *tert*-butyl hydroperoxide consumption (Fig. 1) and 1,2-epoxyoctane formation (Fig. 2)

are observed in the reaction system, as it was expected. It allows us to state all vanadium-containing compounds catalyze the hydroperoxide epoxidation process.

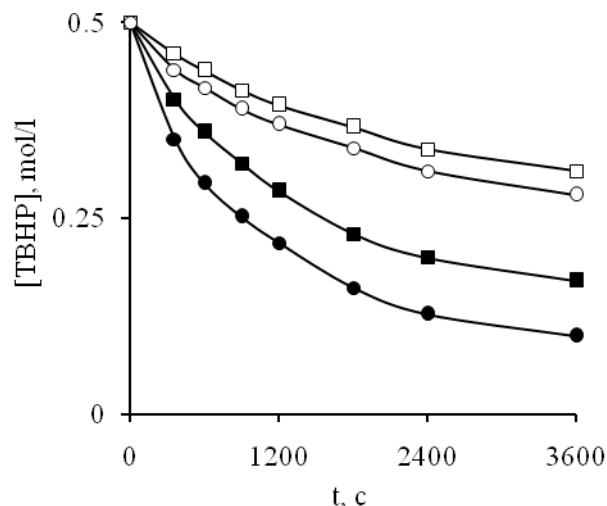


Fig. 1. Kinetic curves for TBHP consumption in the epoxidation reaction of 1-octene by *tert*-butyl hydroperoxide in the presence of: VB_2 (●), VC (■), VSi_2 (○) and V_2O_5 (□)

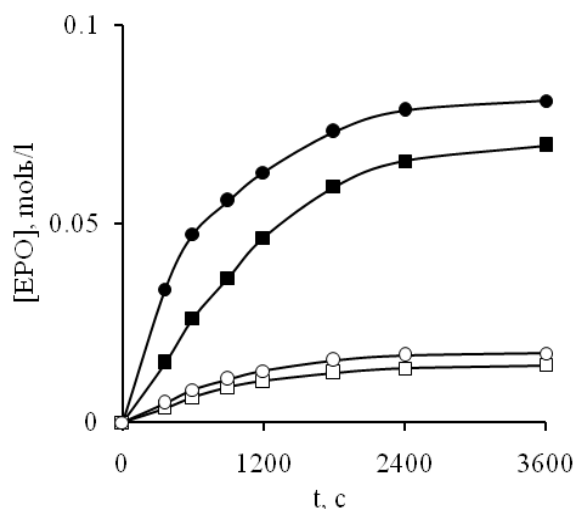


Fig. 2. Kinetic curves for 1,2-epoxy octan eaccumulation during the epoxidation reaction of 1-octene by *tert*-butyl hydroperoxide in the presence of: VB_2 (●), VC (■), VSi_2 (□) and V_2O_5 (○)

The catalytic activity of vanadium compounds in the epoxidation reaction of 1-octene by *tert*-butyl hydroperoxide is different and defined by nature of ligand. It can be seen from Fig. 1 vanadium boride is the most active catalyst as in both *tert*-butyl hydroperoxide consumption process and 1,2-epoxyoctane formation process. In the case of vanadium oxide as

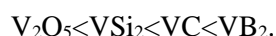
well as vanadium silicide, the value of *tert*-butyl hydroperoxide consumption is low and a little bit better for VSi_2 . Similarly, the amount of formed 1,2-epoxyoctane is small and also slightly higher for vanadium silicide.

According to that VSi_2 and V_2O_5 can be considered as lowly active catalysts of the epoxidation reaction of 1-octene by *tert*-butyl hydroperoxide. Vanadium carbide has an intermediate place between highly active vanadium boride and lowly active vanadium oxide and vanadium silicide. *Tert*-butyl hydroperoxide consumption in the presence of VC is slightly higher than in the presence of VSi_2 and V_2O_5 . While the amount of formed epoxide is significantly increasing and trying to reach the value observed in the case of VB_2 .

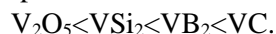
The quantitative parameters of the hydroperoxide epoxidation process such as *tert*-butyl hydroperoxide conversion, selectivity of 1,2-epoxyoctane formation and epoxide yield are calculated and presented in Fig. 3 (reaction time – 40 minutes).

The results given in Fig. 3 demonstrate that the highest value of both hydroperoxide conversion and 1,2-epoxyoctane yield were obtained in the presence of vanadium boride in the hydroperoxide epoxidation reaction. Application of vanadium carbide as a catalyst in epoxidation reaction provides the maximum selectivity of 1,2-epoxyoctane formation. In the case of silicide and vanadium oxide the process parameters are close and low.

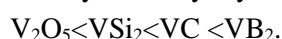
The catalytic activity of investigated vanadium-containing compounds in the process of *tert*-butyl hydroperoxide consumption in the epoxidation reaction of 1-octene varies in the following order:



The catalytic selectivity for 1,2-epoxyoctane formation demonstrated by tested V-catalysts in the hydroperoxide epoxidation reaction varies as:



The studied vanadium compounds can be arranged in the following order in increasing in value of 1,2-epoxycyclooctane yield in the epoxidation reaction of 1-octene by *tert*-butyl hydroperoxide:



The low selectivity of epoxide formation may indicate that vanadium compounds catalyze the *tert*-butyl hydroperoxide decomposition process which is competitive with the epoxidation process for hydroperoxide consumption.

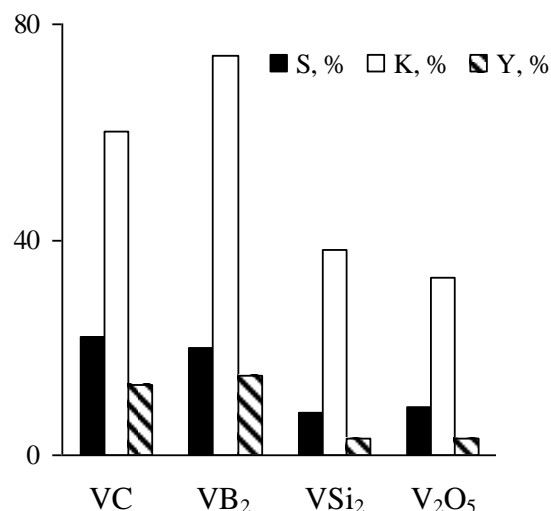


Fig. 3. TBHP conversion, selectivity of 1,2-epoxycyclooctane formation and EPO yield in the epoxidation reaction of 1-octene by *tert*-butyl hydroperoxide in the presence of: VB_2 , VC, VSi_2 and V_2O_5

Fig. 4 demonstrates the kinetic curves for *tert*-butyl hydroperoxide consumption in its decomposition reaction in the presence of vanadium compounds and in the absence of 1-octene in the reaction system.

The same as in the case with hydroperoxide epoxidation of 1-octene, additional experiments have shown that *tert*-butyl hydroperoxide is practically not consumed in the absence of vanadium compounds and 1-octene in the reaction system under the tested conditions, so non-catalytic decomposition of hydroperoxide does not occur.

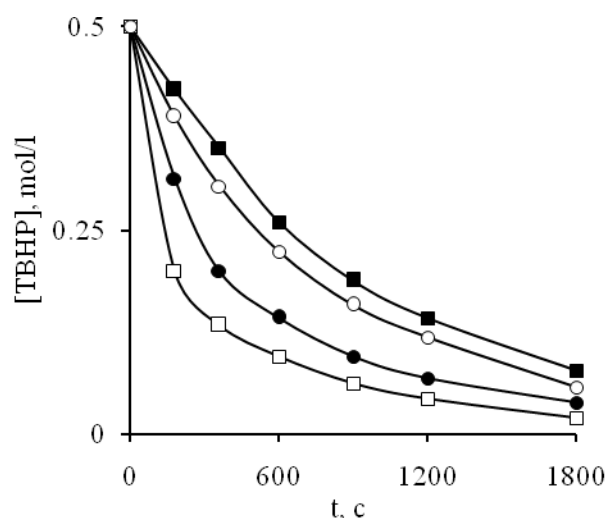


Fig. 4. Kinetic curves for TBHP consumption in the decomposition reaction of *tert*-butyl hydroperoxide in the presence of: VB_2 (●), VC (■), VSi_2 (○) and V_2O_5 (□)

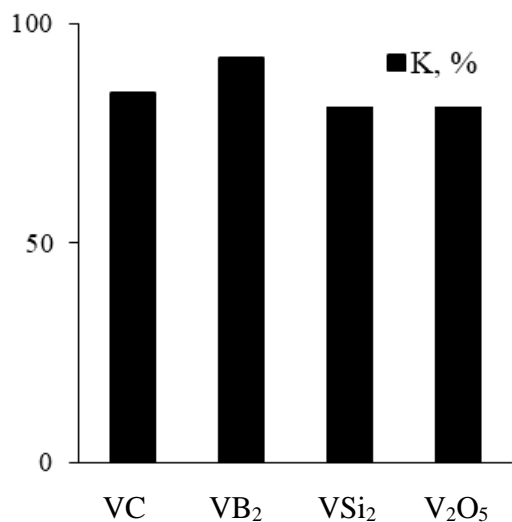


Fig. 5. TBHP conversion in the decomposition reaction of *tert*-butyl hydroperoxide in the presence of: VB₂, VC, VSi₂ and V₂O₅

The most active catalyst of the hydroperoxide decomposition reaction is vanadium oxide, which exhibits the least activity in the epoxidation process. Whereas, in the presence of the most selective catalyst for the 1,2-epoxyoctane formation the lowest value of *tert*-butyl hydroperoxide conversion is observed in decomposition reaction for 20 minutes (Fig. 5).

It is interesting to note that the consumption of *tert*-butyl hydroperoxide occurs more intensively in the absence of 1-octene in the reaction system, namely in the decomposition reaction of hydroperoxide, but not in the reaction of hydroperoxide epoxidation of 1-octene.

The tested vanadium-containing compounds can be arranged in the following order in increasing of their catalytic activity in the process of *tert*-butyl hydroperoxide consumption in the decomposition reaction of this hydroperoxide:



On the base of the activity of vanadium-containing compounds in the formation of 1,2-epoxyoctane in the reaction of hydroperoxide epoxidation and in the *tert*-butyl hydroperoxide decomposition one can conclude that V-catalyst with carbon ligand is the most effective epoxidation catalyst but the least active *tert*-butyl hydroperoxide decomposition catalyst. Whereas catalyst containing oxygen ligand is the most active catalyst for decomposition of *tert*-butyl hydroperoxide and provides the lowest selectivity of epoxidation process.

Conclusions

The catalytic activity of vanadium-containing compounds was investigated in the epoxidation reaction of 1-octene by *tert*-butyl hydroperoxide and the reaction of *tert*-butyl hydroperoxide decomposition. The ligand nature defines the catalytic activity of tested vanadium compounds. The highest selectivity of 1,2-epoxyoctane formation in the reaction of hydroperoxide epoxidation of 1-octene is reached when vanadium carbide is used as a catalyst, whereas the maximum yield of octene epoxide is observed in the case of vanadium boride. The *tert*-butyl hydroperoxide decomposition process occurs most intensively in the presence of vanadium oxide in the reaction system.

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АКТИВНІСТЬ СПОЛУК ВАНАДІЮ У РЕАКЦІЇ ЕПОКСИДУВАННЯ ОКТЕНУ-1 І РОЗКЛАДУ ГІДРОПЕРОКСИДУ ТРЕТ-БУТИЛУ

Досліджено вплив ванадійвмісних сполук як каталізаторів на реакцію епоксидування октену-1 гідропероксидом трет-бутилу та розкладу цього гідропероксиду. Показано, що каталітична активність сполук ванадію залежить від природи ліганда, що входить до складу каталізатора. Встановлено, що борид і карбід ванадію є найактивнішими каталізаторами гідропероксидного епоксидування, тоді як V_2O_5 найактивнішим каталізатором розкладу гідропероксиду трет-бутилу. Найвища селективність утворення 1,2-епоксиоктену спостерігається у разі використання як каталізатора VC.

Ключові слова: епоксидування, каталізатори, ванадійвмісні сполуки, октен-1, гідропероксид трет-бутилу.