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ТЕХНОЛОГІЯ ОРГАНІЧНИХ РЕЧОВИН, ТЕХНОЛОГІЯ ПЕРЕРОБКИ НАФТИ ТА ГАЗУ

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INFLUENCE OF TUNGSTEN COMPOUNDS ON REACTION OF 1-OCTENE EPOXIDATION BY *TERT*-BUTYL HYDROPEROXIDE AND HYDROPEROXIDE DECOMPOSITION

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Catalytic ability of tungsten compounds in the reaction of hydroperoxide epoxidation of 1-octene and *tert*-butyl hydroperoxide decomposition was investigated. It is shown that the nature of ligand has significant effect on the catalytic activity of tungsten compounds in these reactions. It is established that boride and silicide of tungsten are the best choice for epoxidation reaction, whereas tungsten carbide exhibits poor activity. Tungsten boride is also the most active in the hydroxide decomposition reaction.

Key words: epoxidation, decomposition, catalysts, tungsten, 1-octene, *tert*-butyl hydroperoxide.

Introduction

Epoxides belong to an important class of organic heterocyclic compounds [1–3]. They find applications in production of epoxy resins, polymers, surfactants, as well as some pharmaceutics and biologically active compounds. Epoxides are mainly produced in epoxidation reaction of unsaturated compounds. However, in many cases the direct epoxidation of olefins by chemical oxidants, *e.g.* hydrogen peroxide or organic hydroperoxides, appears to be ineffective and accompanied with the formation of unwanted by-products. Activity of oxidants to yield epoxides can be improved by using appropriate catalysts [4, 5].

Today catalysts for epoxidation reaction might be divided into two types: homogeneous and heterogeneous catalysts. The application of the first group of catalysts for epoxidation reaction on a large scale is limited due to the problems arising with catalyst regeneration and recycling, its separation from the reaction products and unavoidable production of toxic waste. Therefore, much attention was focused on the application of the second group of catalysts which are easily separated from the reaction mixture and can be used repeatedly and are more industrially efficient.

Therefore, intensive efforts have been made for a long time to heterogeneous catalysts on the base of transition metals, in particular tungsten, for effective and highly selective synthesis of epoxides from olefins. A novel hierarchical tungsten-substituted silicalite-1 zeolite with the highly interconnected hollow structure (HWS-1) was synthesized and studied as a candidate catalyst for epoxidation of cyclohexene using H_2O_2 with selectivity to epoxide >79% [6]. A series of tungsten-tin bimetallic MFI type zeolites (WSn-MFI) with different Sn and W contents were hydrothermally synthesized and investigated in epoxidation of cyclohexene [7]. It is shown that WSn-MFI-a could efficiently convert cyclohexene to the corresponding epoxide with a high yield of 79% under an optimized reaction condition. A synergistic effect between the W and Sn species should play critical role in improving the catalytic activity and the epoxide selectivity of the bimetallic zeolite catalysts. An efficient heterogeneous catalyst system for the epoxidation of squalene was developed comprising the heterogeneous catalyst $[N(C_6H_{13})_4]_3[PW_4O_8(O_2)_8]$ for the successful epoxidation of squalene with H_2O_2 in *t*-BuOH [8]. The addition of the tetraalkylammonium salt $[N(C_6H_{13})_4]Cl$ and H_2O_2 as the oxidant allowed quantitative epoxidation of squalene. The new catalytic macromolecule POSS-DG2.0-$[W(CO)_3Br_2]$ was tested in the epoxidation of olefins (1-octene, cyclooctene, (S)-limonene, cis-3-hexen-1-ol, trans-3-hexen-1-ol and styrene) and proved to be an active catalyst with conversion rates between 60 and 88 % and high selectivity in the formation of epoxides [9]. Tungstenocene(IV) dichloride was successfully deposited and grafted on the surface of a commercially-available non-ordered silica support (W/SiO_2) showed moderate to good conversion values in the epoxidation of (*R*)-(+)-limonene and methyl oleate (up to 68 %), in the presence of aqueous hydrogen peroxide, with good selectivity to the desired epoxides (63 % and 78 %, respectively) [10].

Aim of the work

The aim of the presented work is to investigate the catalytic effect of tungsten compounds on the epoxidation reaction of 1-octene by *tert*-butyl hydroperoxide as well as the *tert*-butyl hydroperoxide decomposition reaction.

Materials and methods

For investigations were used 1-octene (OK) and 1,2-epoxyoctane (EPO) obtained from Aldrich. Chlorbenzene, reagent chemically pure grade. 1-Octene and chlorbenzene were additionally dried and distilled. *Tert*-butyl hydroperoxide (TBHP) was synthesized by [13]. Tungsten compounds, W_2B_5, WC and WSi_2, were commercial chemicals of chemically pure grade of Donetsk factory of chemical reagents with BET surface area determined by low temperature nitrogen adsorption-desorption method using ASAP 2010: 0,9 m^2/g, 1,0 m^2/g and 1,1 m^2/g, respectively.

The epoxidation reaction as well as decomposition reaction were realized in thermostated glass reactor fitted with a reflux condenser and magnetic stirrer under an argon atmosphere at temperature 383 K in solution of chlorbenzene. Typically, reagents, 1-octene and TBHP, and solvent were loaded into the reactor and heated up to the reaction temperature under stirring. Only then catalyst, tungsten compound, was added and this moment was considered as the reaction start. 1-Octene initial concentration was 3 mol/l, *tert*-butyl hydroperoxide initial concentration was 0,5 mol/l, catalyst content was 3 m^2/l. Samples of reaction mixure were withdrawn in regular interval and analyzed. Hydroperoxide contant was determined by iodometric titration. The reaction mixture were analyzed by chromatographic method. It was established in the blank experiments that TBHP does not decompose and EPO is not formed under the reaction conditions in the absence of the catalyst and.

Results and discussion

Figs. 1 and 2 demonstrate the influence of W-compounds on the epoxidation reaction of 1-octene by *tert*-butyl hydroperoxide. It can be see that all compounds of tungsten effect on both hydroperoxide consumption and epoxide of 1-octene formation. Taking into account that uncatalytic process does not proceeds under the reaction conditions, as was mentioned above, we can colclude that tungsten compounds can find application as catalysts in epoxidation reaction of 1-octene.

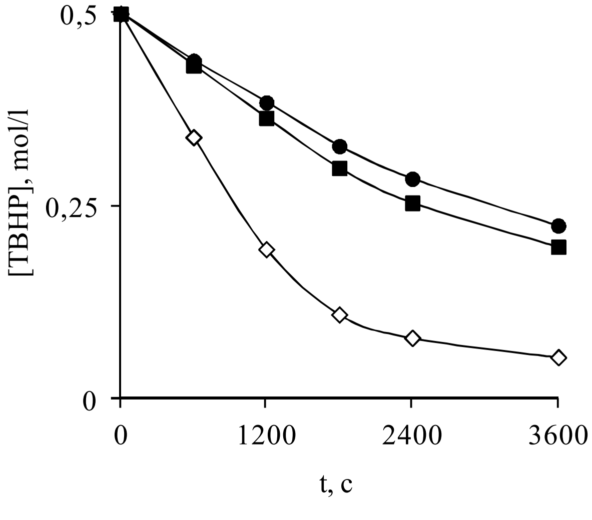

Fig. 1. Kinetic curves for tert-butyl hydroperoxide consumption in the hydroperoxide epoxidation reaction of 1-octene in the presence of: W_2B_5 (■), WC (●) and WSi_2 (◊)

The highest hydroperoxide consumption (Fig. 1) as well as the highest quantity of 1,2-epoxyoctane formation (Fig. 2) is observed in the case of tungsten silicide and the lowest – in the case of tungsten carbide. In the presence of tungsten boride the *tert*-

butyl hydroperoxide consumption is low and a little bit higher than in the presence of WC while amount of formed 1,2-epoxyoctane has intermediate position between WSi_2 and WC.

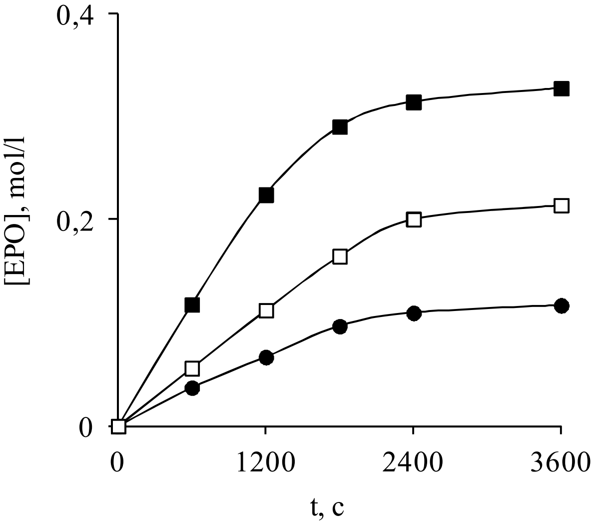

Fig. 2. Kinetic curves for1,2-epoxyoctane accumulation in the epoxidation reaction of 1-octene by tert-butyl hydroperoxide in the presence of: W_2B_5 (□), WC (●) and WSi_2 (■)

Conversion of *tert*-butyl hydroperoxide (K), selectivity of 1,2-epoxycyclooctane formation (S) and yield of 1,2-epoxycyclooctane (Y) were calculated at 30 minutes of reaction proceeding as:

$$K = 100\ \% \cdot [\text{TBHP reacted}] / [\text{TBHP initial}]$$

$$S = 100\ \% \cdot [\text{EPO formed}] / [\text{TBHP reacted}]$$

$$Y = 100\ \% \cdot [\text{EPO formed}] / [\text{TBHP initial}]$$

and presented in Fig. 3.

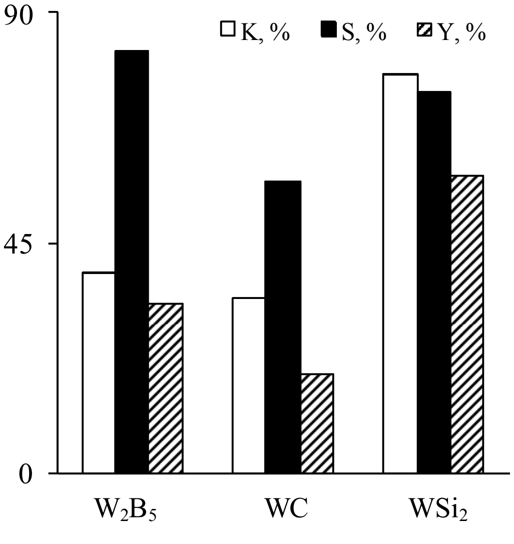

Fig. 3. Catalytic performance of tungsten compounds in the epoxidation reaction of 1-octene by tert-butyl hydroperoxide

The highest conversion of hydroperoxide and epoxide yield are obtained for silicide of tungsten whereas the highest selectivity is observed for tungsten boride (Fig. 3). In the presence of tungsten compound the values of the epoxidation reaction parameters varies as:

TBHP conversion: WC ≤ W_2B_5 < WSi_2;
selectivity for 1,2-epoxyoctane formation:
WC < WSi_2 < W_2B_5;
1,2-epoxycyclooctane yield: WC < W_2B_5 < WSi_2.

Therefore, W-compounds demonstrate different catalytic activity of in the epoxidation reaction which is defined by ligand nature. The best catysts for epoxidation reaction are boride and silicide of tungsten. W_2B_5 is the most selective catalyst whereas WSi_2 favours the epoxide yield. The application of WC in epoxidation reaction is not very reasonable according to low reaction parameters obtained in it's presence.

The presented results show that two competitive process: epoxidation of 1-octene and unproductive decomposition of TBHP, take place in the epoxidation system. The part of hydroperoxide involved in these competitive processes depends on catalyst ligand nature as is shown in Fig. 4. In the presence of WSi_2 the lowest part of TBHP is unreacted whereas more than half of hydroperoxide amount is used productively for epoxide formation. The contrary situation is observed in the case of boride and carbide of tungsten, respectively nealy and more than 60 persent of TBHP amount is not reacted. Moreover in the presence of WC only near half of reacted TBHP is used for epoxide formation and rest is used unproductively. Whereas the lowest part of unproductive consumption of reacted hydroperoxide is observed for W_2B_5.

Accordingly, the decomposition reaction of *tert*-butyl hydroperoxide in the presence of W-compounds and in the absence of 1-octene in the reaction system is also investigated in the same reaction conditions. The results are presented in Figs. 5 and 6. It is seen that in the case of W_2B_5 the TBHP comsumption is the highest and hydroperoxide conversion reachs the value about 70 %. In the same time the effect of WC and WSi_2 is low. The kinetic curves of TBHP consumption as well as the conversion values in their case are closed.

The catalityc activity of W-compounds in the hydroperoxide decomposition reaction is increased in order: WC ≤ WSi_2 < W_2B_5. The most active catalyst of *tert*-butyl hydroperoxide decomposition reaction is tungsten boride.

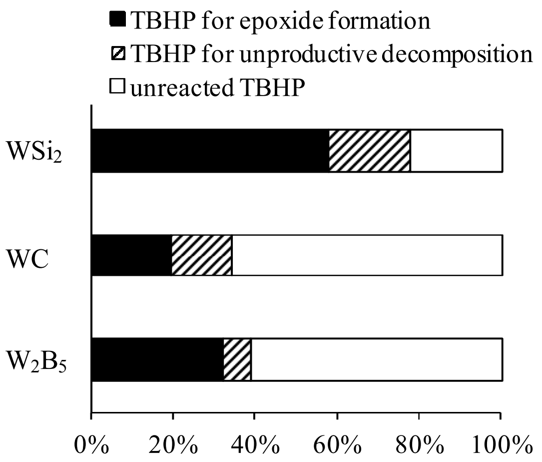

Fig. 4. Dependence of the part of tert-butyl hydroperoxide, consumpted for 1,2-epoxycyclooctane formation and for unproductive decomposition as well as unreacted hydroperoxide on ligand nature of tungsten compounds in the hydroperoxide epoxidation reaction of 1-octene

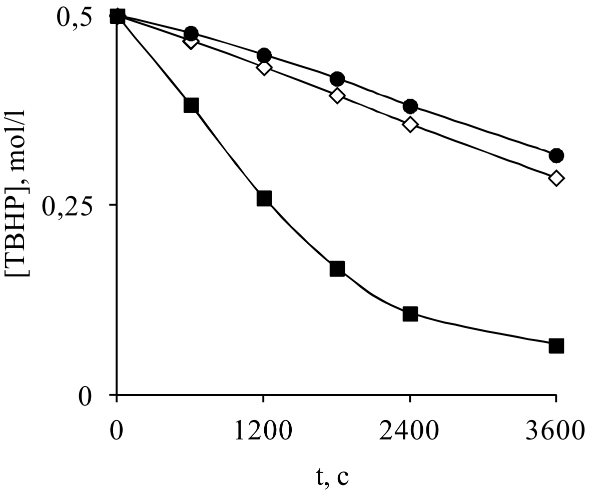

Fig. 5. Kinetic curves for tert-butyl hydroperoxide consumption in the decomposition reaction of this hydroperoxide in the presence of: W_2B_5 (■), WC (●) and WSi_2 (◊)

Based on the obtained results we can state that the most active tungsten catalysts for the epoxidation reaction are silicide and boride. The activity of tungsten carbide is poor in both epoxidation of 1-octene and *tert*-butyl hydroperoxide decomposition reaction. The most intensive proceeding of the decomposition reaction is observed in the case of W_2B_5. So, W-compounds exhibits different activity in the epoxidation and decomposition reaction which defined by ligand nature.

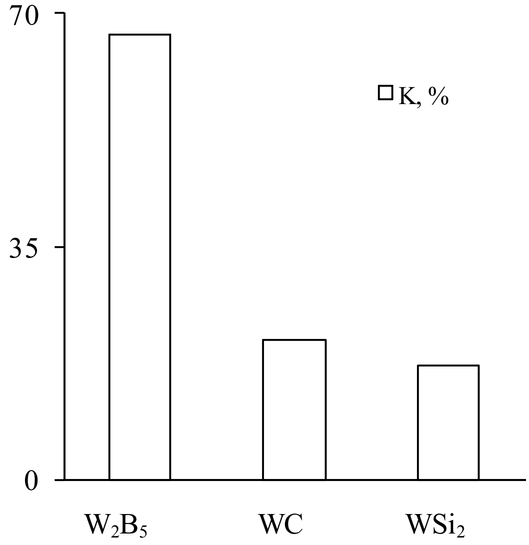

Fig. 6. Influence of ligand nature of tungsten compounds on TBHP conversion in the hydroperoxide decomposition reaction

Conclusions

The catalytic ability of tungsten compounds was investigated in the hydroperoxide epoxidation reaction of 1-octene and the *tert*-butyl hydroperoxide decomposition reaction. The activity of W-catalysts depends on ligand nature. The most preferable catalysts for epoxidation reaction are W-compounds containing Si and B ligands, namely WSi_2 and W_2B_5. Application of tungsten boride allows reachs the highest selectivity whereas WSi_2 leads to highest epoxide yield. W_2B_5 is also the most active in the hydroperoxide decomposition reaction. W-compound containing C ligand, WC, is slightly active in both epoxidation and decomposition reactions.

References

1. Yudin A. K. (2006). *Aziridines and Epoxides in Organic Synthesis*. Wiley-VCH, Weinheim, Germany. doi: 10.1002/3527607862

2. Marco-Contelles J., Molina M. T., Anjum S. (2004). Naturally occurring cyclohexane epoxides: Sources, biological activities and synthesis. *Chemical Reviews*, 104(6), 2857–2899. doi: 10.1021/cr980013j

3. Emami M., Bikas R., Noshiranzadeh N., Kozakiewicz A., Lis T. (2020). Cu(II)-Hydrazide coordination compound supported on silica gel as an efficient and recyclable heterogeneous catalyst for green click synthesis of β-hydroxy-1,2,3-triazoles in water. *ACS Omega,* 5, 13344–13357. doi: 10.1021/acsomega.0c01491

4. Arends I. W. C. E., Sheldon R. A. (2001). Activities and stabilities of heterogeneous catalysts in selective liquid phase oxidations: recent developments. *Applied Catalysis A*, 212(1–2), 175–187. doi: 10.1016/S0926-860X(00)00855-3

5. Xia Q. H., Ge H. Q., Ye C. P., Liu Z. M., Su K. X. (2005). Advances in homogeneous and heterogeneous catalytic asymmetric epoxidation. *Chemical Reviews*, 105(5), 1603–1662. doi: 10.1021/cr0406458

6. Wang X., You Q., Wu Y., Bi C., Chen H., Dai C., Hao Q., Zhang J., Ma X. (2021) Tungsten-substituted Silicalite-1 with an interconnected hollow structure for catalytic epoxidation of cyclohexene. *Microporous and Mesoporous Materials*, 317, 111028. doi: 10.1016/j.micromeso.2021.111028

7. Zhang H., Yang X., Song X., Chang X., Jia M. (2020) Hydrothermal synthesis of tungsten-tin bimetallic MFI type zeolites and their catalytic properties for cyclohexene epoxidation. *Microporous and Mesoporous Materials*, 303, 110277. doi: 10.1016/j.micromeso.2021.110277

8. Kawashima H., Okuda Y., Kijima M., Fujitani T., Choi J.-C. (2020) Epoxidation of microalgal biomass-derived squalene with hydrogen peroxide using solid heterogeneous tungsten-based catalyst. *Tetrahedron*, 76(16), 131109. doi: 10.1016/j.tet.2020.131109

9. Vieira E.G., Filho N.L.D. (2017) Epoxidation of olefins using a novel synthesized tungsten dendritic catalyst. *Materials Chemistry and Physics*, 201(1), 262–270. doi: 10.1016/j.matchemphys.2017.08.045

10. Bisio C., Gallo A., Psaro R, Tiozzo C., Guidotti M., Carniato F. (2019) Tungstenocene-grafted silica catalysts for the selective epoxidation of alkenes. *Applied Catalysis A: General*, 581, 133–142. doi: 10.1016/j.apcata.2019.05.027

11. Milas N. A., Surgenor D. M. (1946). Studies in organic peroxides. VIII. t-Butyl hydroperoxide and di-t-butyl peroxide. *Journal of the American Chemical Society*, 68(2), 205-208. doi: 10.1021/ja01206a017

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ВПЛИВ СПОЛУК ВОЛЬФРАМУ НА РЕАКЦІЮ ЕПОКСИДУВАННЯ ОКТЕНУ-1 *ТРЕТ*-БУТИЛГІДРОПЕРОКСИДОМ І РОЗКЛАДУ ГІДРОПЕРОКСИДУ

Досліджено каталітичну здатність сполук вольфраму в реакції гідропероксидного епоксидування октену-1 і розкладу гідропероксиду *трет*-бутилу. Показано, що природа ліганда істотно впливає на каталітичну активність сполук вольфраму в цих реакціях. Встановлено, що борид і силіцид вольфраму є найкращими для реакції епоксидування, тоді як карбід вольфраму проявляє низьку активність. Борид вольфраму є також найактивніший у реакції розкладу гідропероксиду.

Ключові слова: епоксидування, розклад, каталізатори, вольфрам, октен-1, гідропероксид *трет*-бутилу.