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THE STUDIES ON COMPLEX FORMATION OF METAL BORIDES IN THE REACTION SYSTEM OF EPOXIDATION OF 1-OCTENE WITH TERT-BUTYL HYDROPEROXIDE BY IR SPECTROSCOPY

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Abstract. The complex formation of molybdenum and vanadium borides in the reaction system of 1-octene epoxidation with *tert*-butyl hydroperoxide by infrared spectroscopic analysis was studied. It was shown that 1-octene forms complex with metal moiety in the case of molybdenum boride and with boron moiety in the case of vanadium boride.

Keywords: infrared spectroscopy catalyst, epoxidation, olefin, hydroperoxide

1. Introduction

Epoxides are an important class of organic compounds which are widely used as intermediate reagents in the organic synthesis of various oxygenated compounds, in the production of polyurethane resins, surfactants, polymers, biologically active compounds, etc. [1–4]. One of the effective methods of the epoxides synthesis is catalytic epoxidation reaction of olefin with hydroperoxides.

The formation of two types of double complexes is possible in the reaction system of hydroperoxide epoxidation, which contains hydroperoxide, olefin and catalyst – hydroperoxide-catalyst and olefin-catalyst complexes. It was shown by the kinetic method of investigation in [5-8], that a primary complex which is responsible for the formation of epoxide is olefin-catalyst complex. The equilibrium exists between the complexes of hydroperoxide-catalyst and olefin-catalyst:

$$\text{Hydroperoxide-Catalyst} + \text{Olefin} \rightleftarrows$$
$$\rightleftarrows \text{Olefin-Catalyst} + \text{Hydroperoxide}$$
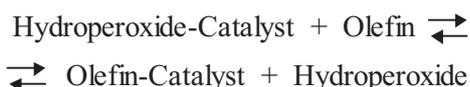
The selectivity of epoxide formation is higher when this equilibrium is more accented toward formation of olefin-catalyst complex.

In this work, using infrared (IR) spectroscopy, we investigated the complex formation processes which occur on the surface of MoB and VB heterogeneous catalysts at their interaction with the components of 1-octene epoxidation with *tert*-butyl hydroperoxide (TBHP) reaction system for confirmation of the conclusions received by the kinetic way.

2. Experimental

Commercial 1-octene of pure grade was additionally purified by distillation. TBHP was synthesized by the procedure described in [5]. The catalysts were commercial chemicals of a chemically pure grade. Chlorbenzene of reagent pure grade used as a solvent was additionally dried and distilled. The epoxidation process was carried out in an argon atmosphere in a thermostated glass reactor fitted with a reflux condenser and a magnetic stirrer as well as constant temperature jacket to keep the temperature constant within ± 0.1 K.

The reaction mixture was analyzed using a Tsvet 100 chromatograph with 3 m long column packed with 10% Apieson L on Chromaton N-AW. The column temperature was 410 K and the carrier gas (hydrogen) flow rate was 3.6 l/h. The hydroperoxide concentration was determined by iodometric titration.

The IR spectra of initial catalysts as well as the catalysts after their interaction with 1-octene or TBHP were recorded by SPECORD-80 spectrometer in 4000-400 cm^{-1} range using pressed KBr pellets. The catalyst samples treated by reagents were prepared in such a way: the catalyst was added to the solution of 1-octene or TBHP (the concentrations of 1-octene and TBHP were equal to the concentrations of these compounds in the epoxidation reaction mixture). This mixture was stirred for the period which was equal to the time of the catalytic epoxidation reaction. Then the catalyst was separated from this mixture, pressed with KBr and IR spectra were recorded.

3. Results and Discussion

In Fig. 1 the kinetic curves of TBHP consumption and 1,2-epoxyoctane accumulation in the process of 1-octene epoxidation with TBHP in the presence of MoB and VB are shown. One can see, that the amount of epoxide which is formed at the identical TBHP consumption is almost 3 times less in the case of VB than that in the case of MoB. It indicates a considerably greater contribution of unproductive decomposition process of TBHP in comparison with the consumption for epoxide formation in the case of VB. In accordance with [5], this effect must be connected with the much greater stability of hydroperoxide-catalyst complex in comparison with olefin-catalyst complex in VB case.

The IR spectra of initial molybdenum and vanadium borides as well as the spectra of these catalysts after their interaction with 1-octene and TBHP are shown in Figs. 2 and 3. One can see that initial MoB (Fig. 2, spectrum 3) and VB (Fig. 3, spectrum 3) spectra have intensive absorption bands at 717, 1428, 3217, 3399 cm^{-1} and at 1195, 1421, 1629, 3231, 3410 cm^{-1} respectively. The intensity and absorption frequency of these bands are changing after interaction of the catalyst with components of the reaction system.
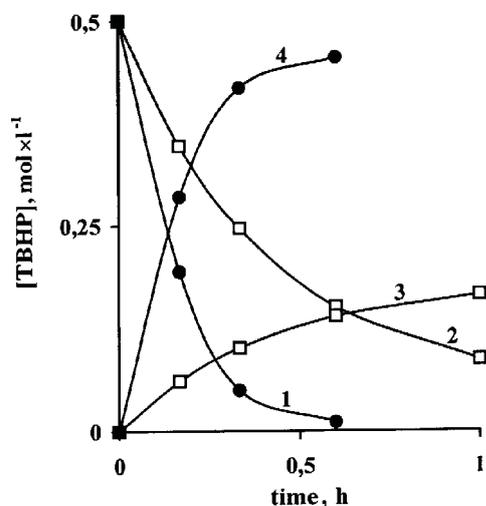

Fig. 1. TBHP (1, 2) and epoxyoctane (EP) (3, 4) concentrations as the functions of reaction time in the epoxidation reaction of 1-octene with TBHP in the presence of MoB (1, 4) and VB (2, 3). Reaction conditions: T = 363 K, octene 2.5 mol/l, catalyst 10 g/l.

The IR spectra of initial VB after its interaction with TBHP (Fig. 3, spectrum 1) and 1-octene (Fig. 3, spectrum 2) are changing and become similar to each other. They contain absorption bands at 1195, 1448 (with 1-octene), 1456 (with TBHP) and 3212 cm^{-1}. The comparison of VB spectra 3 with 1 and 2 suggests that intensity of absorption band at 1195 increases and the band at 1421 (spectrum 3)

shifts to 1448 (spectrum 2) and 1456 (spectrum 1). The band intensity at 3410 (spectrum 3) decreases and this band is overlapped by the band at 3212 (spectra 1 and 2). The band at 3212 shifts by 19 cm^{-1} in comparison with this band in spectrum 3.

The IR spectra of MoB after their interaction with TBHP (Fig. 2, spectrum 1) and 1-octene (Fig. 2, spectrum 2) are changing too. But in contrast to VB spectra, MoB spectra 1 and 2 are differed considerably. After their interaction with 1-octene (Fig. 2, spectrum 2) MoB spectrum contains absorption bands at 1385, 1637 and 3426 cm^{-1}. The band at 3217 in spectrum 3 overlaps that in spectrum 2 by a stronger band at 3426 cm^{-1}. Band at 1637 appears in spectrum 2 together with band at 3426, but it is very weak in spectrum 3.
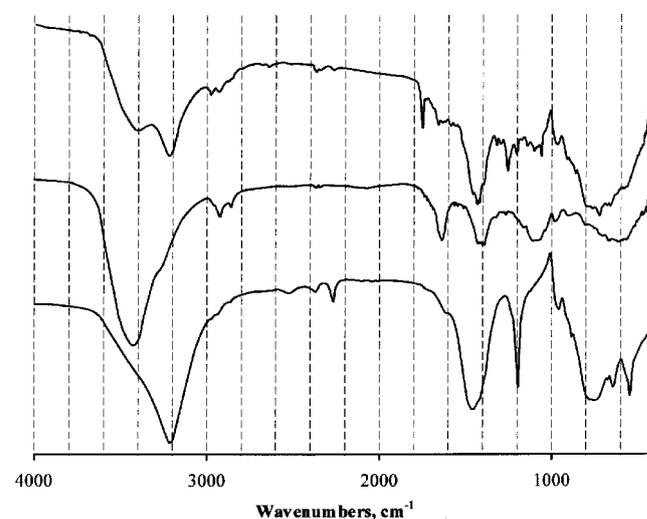

Fig. 2. IR spectra of the initial MoB (3) and MoB after their interaction with TBHP (1) and 1-octene (2).

After the interaction with TBHP (Fig. 2, spectrum 1) absorption bands at 1195, 1456 and 3214 cm^{-1} are observed in MoB spectrum. In comparison with spectrum of the initial MoB (spectrum 3) the band intensity at 1195 appears in spectrum 1 which is also presented in VB spectra too, the band at 3214 cm^{-1} increases and overlaps the band at 3399 which is in spectrum 3. In comparison with spectrum 3 the band intensity at 1456 cm^{-1} increases with the increase of the band intensity at 3214 cm^{-1}.

From the spectra in Figs. 2 and 3 one can see two groups of mutual connection absorption bands at about 3400 and 1640 as well as at 3220 and 1400 cm^{-1}. Increasing intensity of one of the bands in the group at higher wavenumbers at about 3400 or 3220 results in increasing intensity of respective lower wavenumbers at about 1640 or 1400 cm^{-1}. This fact indicates the presence of two centres on MoB and VB surfaces which can react with reagents of epoxidation reaction system. The centre

which has absorbtion band at about 3220 and 1400 cm^{-1} reacts in case of MoB with TBHP interaction, while the centre which has absorption bands at about 3400 and 1640 cm^{-1} reacts with 1-octene. Only one centre which absorbs at about 3220 and 1400 cm^{-1} reacts in case of VB with TBHP and 1-octene interaction, as it can be seen from the similar VB spectra after its interaction with TBHP and 1-octene (Fig. 3, spectra 1 and 2).

The wide absorption bands at about 3400 and 3220 cm^{-1} are assigned to stretching vibrations of –OH bonds and bands at about 1640 and 1400 cm^{-1} – to the deformation vibrations of –OH bonds [9]. The peak at about 1400 cm^{-1} may be assigned to stretching vibrations of B-O bond [10] and the corresponding band at about 3220 may be assigned to the stretching vibrations of –OH group bonded with boron.

The second group of the absorption bands at around 3400 and 1640 cm^{-1} can be assigned to the absorption of –OH group bonded with the metal atom of boride. The comparison of obtained results of epoxidation process presented in Fig.1 with the results of spectra analysis suggests that the high selectivity of the epoxidation process in the presence of MoB may be connected with the formation of olefin-catalyst complex on the surface of this boride. In case of VB olefin interacts mainly with boron moiety, mainly results in nonproductive decomposition of TBHP.
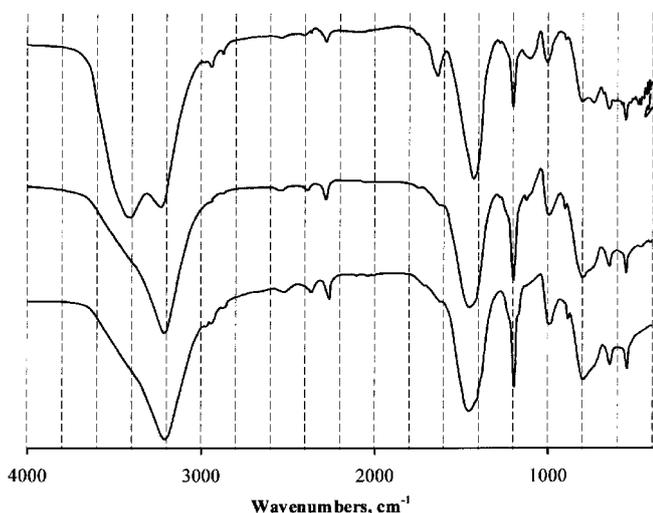

Fig. 3. IR spectra of the initial VB (3) and VB after their interaction with TBHP (1) and 1-octene (2).

4. Conclusions

Thus, the obtained results can confirm the preliminary conclusion based on kinetic results that the epoxidation process proceeds through the primary formation of the olefin-catalyst complex.

The obtained spectrum data indicate that olefin must form the complex with the metal moiety of metal compound for the selective convertion to epoxide,.

Further investigations will be focused on studying of complex formation on the surface of other catalysts in the hydroperoxide epoxidation reaction system by means of infrared spectroscopy.

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ВИВЧЕННЯ КОМПЛЕКСОУТВОРЕННЯ БОРИДІВ МЕТАЛІВ У РЕАКЦІЙНІЙ СИСТЕМІ ЕПОКСИДУВАННЯ ОКТЕНУ-1 ГІДРОПЕРОКСИДОМ ТРЕТБУТИЛУ МЕТОДОМ ІЧ СПЕКТРОСКОПІЇ

Анотація. Вивчено комплексоутворення боридів молібдену і ванадію в реакційній системі епоксидування октену-1 гідропероксидом трет-бутилу методом інфрачервоної спектроскопії. Показано, що октен-1 утворює комплекс з металевою складовою у випадку бориду молібдену і з боридною складовою у випадку бориду ванадію.

Ключові слова: інфрачервона спектроскопія, каталізатор, епоксидування, олефін, гідропероксид