

Catalytic Oxidation of Organic Compounds in the Presence of Crown-ethers

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Researches of crown ether (CE) presence influence on processes of cyclohexane and other alkyaromatic hydrocarbons oxidation were made. These researches showed that presence of CE in catalytic system can variously impact not only speed of the process but also ratios of basic and side products. This article contains results and discussion of results. It also contains graphical material that represents obtained information

1. Introduction

Modern research shows that the most effective in the oxidation of hydrocarbons is catalytic system, which along with salts of metals of variable valency (mvv) contain compounds that may act as electron-donor-acceptor or electrno ligands [1, 2]. Use of such catalytic systems are an effective way of influencing both the speed and selectivity in oxidation processes of different classes of hydrocarbons [3, 4 - 6, 7]. There are known major research of cyclohexane and alkyaromatic hydrocarbons oxidation in the presence of catalytic systems which contains an organic salt of cobalt salts of perfluorooxisulfo acids (SPFSA), which show elektrono-acceptor properties. The use of such catalytic systems allows increasing responsiveness and improving selectivity for desired products, and changing the ratio between the target products of oxidation [3]. Crown ethers (CE) in contrast to SPFSA are electron-donor ligands. So it was logical to investigate their effect on the above processes. This would get the information needed to predict the influence of organic additives of this or other nature for conversion of hydrocarbons and selective formation of desired products, and would also explain the mechanism of such catalytic systems in some stages of oxidation.

2. Experimental

Liquid oxidation of hydrocarbons (cyclohexane, toluene, xylene) ,in the presence of catalytic systems salt of mvv – CE, was studied at temperatures of 383-438K and pressure of 0,1-1,1 MPa. The concentration of mvv salt was $(1,0-5,0) \cdot 10^{-4}$ mol / l at the oxidation of cyclohexane and $(1,0-3,0) \cdot 10^{-3}$ mol / l at oxidation of alkyaromatic hydrocarbons. Molar ratio [mvv salt] / [CE] changed in the range from 10/1 to 1/1. The

influence of these CE: 15-crown-5 (15-CA-5), 18-crown-6 (18-CA-6), dibenzo-18-crown-6 (DBCR) dyazo-18-crown-6 (DACR) was studied. As a variable valence metal salt were used organic salts of cobalt : oxidation of cyclohexane – naftenate of cobalt (NC), during oxidation of alkylaromatic hydrocarbons - cobalt acetate (AC).

Oxidation rate was calculated as the average speed of carbon expense for certain time interval. It was defined as the ratio of carbon concentration change to time interval, during which this change took place.

3. Results and Discussion

Oxidation of cyclohexane in the presence of catalytic systems NC-CE showed that the use of oxygen containing CE leads to an increase in rate of oxidation of cyclohexane (Fig. 1). At the same time, the use of nitrogen containing CE does not significant impact on the rate of oxidation, in addition its presence significantly increases induction period. During oxidation of alkylaromatic hydrocarbons hydrocarbon oxidation rate increases in the application of oxygen containigand virtually unchanged in the presence DACR (Fig. 2). These close results suggests that the influence of catalytic systems that contain CE, on the rate of oxidation of hydrocarbons significantly depends on CE nature and practically does not depend on the nature of oxidative substrate.

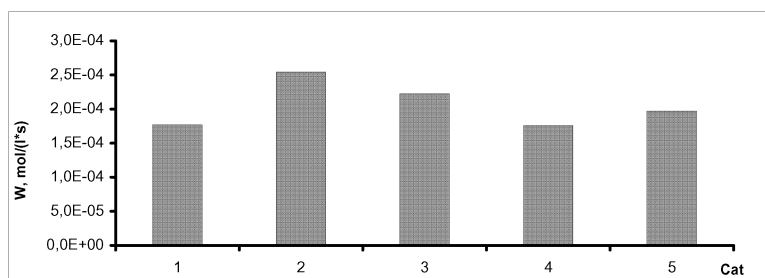


Figure 1: The influence of CE nature on the rate of cyclohexane oxidation. 1 - NC 2 - NC-15-CA-5, 3 - NC-18-CA-6, 4 - NC-DACR, 5 - NC-DBCR. $T = 413K$, $P = 1.0 MPa$.

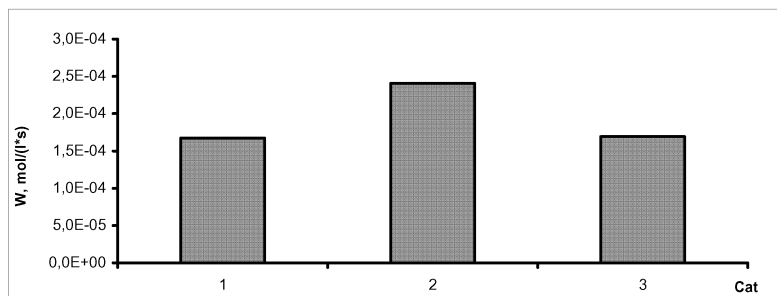


Figure 2 The influence of CE nature on the rate of toluene oxidation. 1 - NC 2 - NC-DBCR, 3 - NC-DACR. $T = 423K$, $R = 0,4 MPa$.

The presence of catalytic systems consisting of CE also affects the speed of accumulation and selectivity of formation of cyclohexane oxidation products and the ratio CON / COL: the presence of CE within the catalytic system leads to significant speed increase of HPCN accumulation and to decrease of accumulation ratio rates OL / OH . This is particularly evident in the presence of unsubstituted oxygen-containing CE - CR-15-18-5 and CA-6. Taking to consider results of [3] we can conclude that that organic additives, which have elektrono-acceptor nature lead to an increase in the ratio of OL / OH, and additives, which have electron-donor nature - to reduce in it.

Unlike the cyclohexane oxidation use of CE during alkylaromatic hydrocarbon oxidation leads to increase of alcohol content, not the aldehyde, while using elektrono-acceptor additives leads to an increase in the content of aldehyde in reaction system [8]. What can express the assumption that the influence of organic additives on the composition of reaction products also depends on the nature of oxidative substrate.

Given the possibility of formation of complexes between CE and cations in different ratios (2 / 1, 3 / 2, 1 / 1) [12] (Fig. 3), which can affect the catalyst activity, influence of the ratio [salt mvv] / [CE] to the oxidation of hydrocarbons was studied.

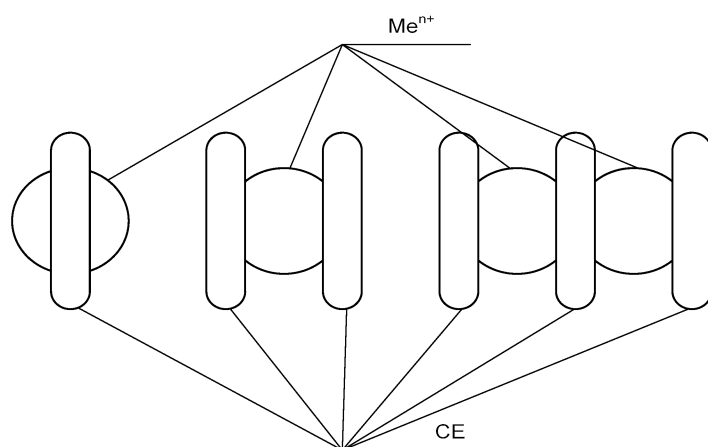


Figure 3: Variants of complexes between the cation and CE mvv

Studies have shown that increasing of CE content within the catalytic system leads to a significant decrease of cyclohexane oxidation speed and increase of induction period. Slow oxidation of cyclohexane with increasing content of CE can be attributed to almost complete complexation, and the inclusion of a large (or even all) of these mvv ions in complexes that are stable, and probably affect the valence transitions of mvv salts (eg, $\text{Co}^{2+} \leftrightarrow \text{Co}^{3+}$) may adversely affect the speed of chains initiation. The increase of CE also leads to virtually complete leveling of CE impact on the composition of reaction mixture: the results are close to those observed in the presence of NC. Reduction of CE can get better results than in the presence of NC, but slightly worse than the ratio 5 / 1. During alkylaromatic hydrocarbons oxidation in the presence of catalytic systems containing CE, was found that with increasing of CE content is also observed decrease of hydrocarbons oxidation rate. Is established that the toluene

oxidation rate from concentration of DACR curve has clearly expressed extreme character. Optimal ratio of $\text{Co}(\text{OAc})_2$: DACR, under which is achieved a maximum speed of toluene oxidation, is 5:1 (mol.). Under p-xylene oxidation change of the ratio AK / CE in a rather wide limits has on the ratio between aldehyde and alcohol. However, at a ratio of AK / CE 1 / 2 significantly increases the content of aldehyde in the reaction mixture, suggesting the inclusion of the basic structure of AK in complex with CE, and the fact that this complex affects on the relationship between the reactions of basic products creation.

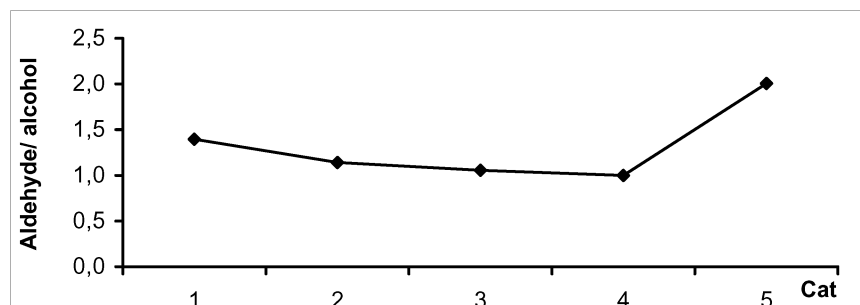
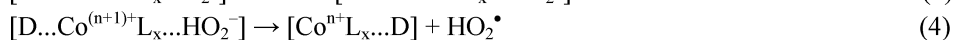
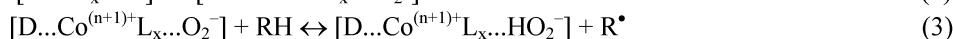


Figure 4: Influence of the ratio AK / DBCR the ratio of aldehyde / alcohol, xylene oxidation. 1 - without DBCR, 2 - 5 / 1, 3 - 3 / 1, 4 - 2,5 / 1, 5 - 1 / 2. $T = 393\text{K}$, $R = 0,1\text{ MPa}$.

The results also showed that the effect of catalytic systems that contain CE, more effectively appeared during reducing of NC concentration. The use of catalytic systems NC - CE with a lower concentration of smvv enables besides increasing the total selectivity of the oxidation process for the targeted products, to achieve improvement of conversion for the same period. Thus, we can assume that CE is an activator of origin chain reactions of hydrocarbons oxidation processes and the activation scheme will involve complex formation between mvv ion and macrocycle D [8]:



Participation of formed complex in the initiation of oxidation, apparently, is activation by it of oxygen and substrate for the reactions:



However, it is known that CE can form complexes not only with spherical substrates (metal cations), but adducts - with neutral substrates, which incorporate structural elements of the C=C, -N, O-O, O, as evidenced by X-ray analysis and NMR spectra [9]. Therefore, we cannot assert that the role of macrocyclic ligands additives in catalytic

alkylaromatic hydrocarbons oxidation is limited by their participation in the emergence of chains.

It is known that the reaction between peroxide radicals from mvv cation in lower or higher degrees of oxidation determines the quantitative composition of oxidation products: under Catalysis of cobalt cations in the first case produced only OL, in the latter - either COL or CON [10]:

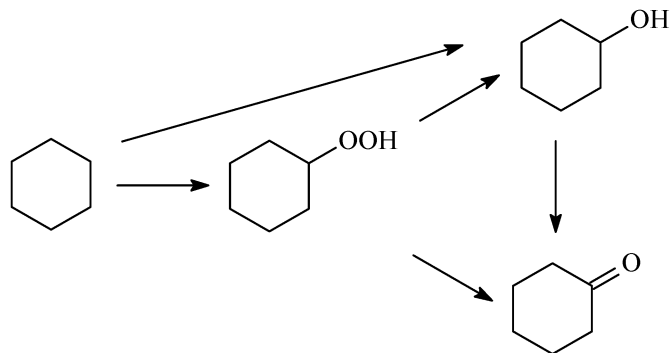


Figure 8: Scheme of formation of major products of cyclohexane oxidation

Thus, we can assume that in the case of electron-donor catalyst additives increases the share of reaction 6, but using electron-acceptor - the share of reaction 5. This results may indicate that organic additives can affect not only embryonic chain and activation of oxygen and substrate, but also change the relationship between forms of existence of catalyst in a reaction mixture, which in turn leads to changes in the ratio between the products of oxidation.

4. Conclusion

Therefore, we can assume that the use of electron-donor compounds leads to an increase in the share of reaction mixture Co^{3+} than Co^{2+} . Whereas the increase of selectivity for cyclohexanone in the presence of CE in most cases accompanied by simultaneous increase in selectivity for cyclohexyl hydroperoxide, it can be explained by the increasing proportion of products (OL, especially ON), formed from peroxide RO_2^\bullet radicals by reaction (5) and (6) passing cyclohexyl hydroperoxide stage (Fig. 8).

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