

Determination of the catalytic complexes structure in the cyclohexane oxidation

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Abstract – A spectral analysis of catalytic solutions based on cobalt naphthenate in cyclohexanone with additives of ethanol and glycine for the cyclohexane oxidation process was conducted.

Key words – oxidation, catalyst, cyclohexane, complexes.

I. Introduction

Using different nature organic modifiers in the cyclohexane (CHX) oxidation in the presence of cobalt naphthenate (CoNph) significantly affects both the composition of the products and the oxidation rate [1]. This effect is associated with participation additives in creation of the intermediate complexes and associates with a catalyst and the oxidation products [2]. For testing these assumptions were made solutions spectral study of complex catalytic systems.

II. Results and discussion

After analyzing the results of studies of the cyclohexane oxidation effects of binary catalytic systems of different nature using, we see that in the presence of additives to CoNph of ethanol (ET) and glycine (GC) there are significant changes in the products composition and the speed of the process at different stages of oxidation (Table. 1).

The data obtained using two catalysts concludes that the nature of these additives (NC + NC + ET and GC) on the selectivity of the process is similar. The presence of additives leads to minor changes of amount of cyclohexyl hydroperoxide (CHP) in the oxidate; to a significant reduction of selectivity values of acids and esters; and to increasing of the aim products concentration – cyclohexanone (CON) and cyclohexanol (COL) – with shifting of the value [COL/CON] towards accumulation of the alcohol. The influence of the speed is multidirectional – ET speeds up and GC slows down the process, relative to CoNph.

The nature of the catalytic systems, which include different nature alcohols and amino acids is associated with the formation of complex compounds or ionic associates involving functional groups of additives with molecule of metal containing catalyst. To support this theory a spectral analysis the solutions of the catalytic systems was conducted.

IR-spectroscopy of the analyzed colloidal solutions catalytic systems was carried out using a spectrometer Specord M-80 in the cell thickness of 0,2 mm. Analysis

of the spectra was based on the tables of characteristic absorption frequencies.

TABLE 1

OXIDATION INDICATORS OF CYCLOHEXANE WITH THE ORGANIC MODIFIERS USE (CONVERSION VALUE AT X ~ 4%)

T = 413 K, P = 1,0 MPA, C(CoNph) = 5,0 × 10⁻⁴ MOL/L

X, %	τ, min	S(CHP1), %	S(A2), %	S(ET3), %	S(COL4),	S(CON5), %	W _{cep} × 10 ³ , mol/l·sec	[COL/CON]	S _{int} , %
CoNph									
4,00	50	10,40	19,62	5,94	37,92	26,11	0,12	1,45	76,42
CoNph – Ethanol									
4,03	40	11,78	4,30	0,00	56,52	27,40	0,16	2,06	95,69
CoNph + Glycine									
3,56	60	9,29	6,44	0,00	54,10	30,17	0,09	1,79	93,56

Note: ¹ cyclohexyl hydroperoxide; ² acids, ³ esters, ⁴ cyclohexanol, cyclohexanone, ⁵ aim products

CON was used as a solvent, which in conditions of the oxidation process is presented in the reaction environment, as well as cobalt naphthenate, which under normal conditions is better soluble than CHX and COL. The concentration of variable valence metal salt (VVM) in the test solutions was 5,0 • 10⁻⁵ mol/l. The total concentration of the catalyst solution was 5% (mass.). The relationship between the components of the catalyst system was [CoNph : Additive] = (1: 1) (mass.).

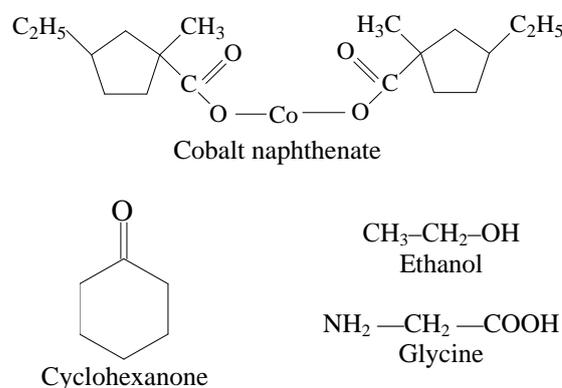


Fig. 1. The structure of the catalytic systems components

Comparing IR visible spectrum of prepared catalytic solutions with the spectrum of CoNph solution we are seeing some significant changes in the absorption bands at certain frequencies (Table 2).

There is no absorption at wavelengths 3300-2800 cm⁻¹, in the sample (CON + CoNph + ET) and there is a wide peak in the range 3700-3100 cm⁻¹; and there are two wide peaks within the 3700-3500 cm⁻¹ and 3300-2800 cm⁻¹ in the samples (CON + CoNph) and (CON + CoNph + GC) corresponding to the OH-groups in complexes with hydrogen bond.

In the sample (CON + CoNph + GC) there is a large peak at 1296 cm⁻¹ and a small peak at 1260 cm⁻¹, when in the sample (CON + CoNph) at 1296 cm⁻¹ it's small and 1260 cm⁻¹ – large.

TABLE 2

THE INFRARED SPECTROGRAPHS RESULTS
OF THE CATALYTIC SOLUTIONS

CoNph + CON		CoNph + CON + GC		CoNph + CON + GC*		CoNph + CON + ET	
$\nu, \delta, \text{cm}^{-1}$	group	$\nu, \delta, \text{cm}^{-1}$	group	$\nu, \delta, \text{cm}^{-1}$	group	$\nu, \delta, \text{cm}^{-1}$	group
–	–	992	-C-O-	992 ⁵	-C-O-	–	–
–	–	–	–	920 ⁷	C-O-C	–	–
		1040	C-OH	1040	-C-OH ³		
1260 ¹	-CH ₃	1260 ²	-CH ₃	1260	-CH ₃	1260 ³	-CH ₃
1296 ²	C-H	1296 ¹	C-H	1296	C-H	1296 ³	C-H
–	–	1664	-C=C-	1664	-C=C-	–	–
1640	C=O	1640 ³	C=O	1640	C=O	1640 ³	C=O
3300-2800	OH...H	3300-2800	OH...H	3300-2800 ⁴	OH...H	–	–
3700-3500	–	3700-3500	-OH	3700-3500	-OH	–	–
–	–	–	–	–	–	3700-3100 ⁶	-OH, OH...H

Note: ¹ big, ² small, ³ increases, ⁴ decreases, ⁵ shifted, ⁶ appears (wide), ⁷ appeared, * (CoNph + CON + GC) solution after heating $\tau = 10$ min. at $T = 413$ K.

The peak at 1296 cm^{-1} corresponding to absorption of C-H in alkanes and has increased by CH₂ presence in amino acid. Intensity of absorption in the sample (CON + CoNph + GC) have been increased at 1640 cm^{-1} compared to (CON + CoNph), which corresponds to the C=O in amino acids. The peak in 1664 cm^{-1} , which corresponds to -C=C- in (CON + CoNph + GC) increased as a result of possible interactions.

After additive of ethanol – sample (CON + CoNph + ET) – in the IR spectra peaks become sharpest and more expressed, which can be explained by the formation of more polar molecules – micelles.

After heating (sample (CON + CoNph + GC)) a peak appears at 920 cm^{-1} , corresponding to the C-O-C bonds – probably was held the interaction between the components of the catalytic solution. Maximum of the absorption (at 992 cm^{-1}) has been shifted toward longer wavelengths, which corresponds to C-O.

After heating most of the hydrogen bonds have been destroyed – there is less peaks at $3400\text{-}3000 \text{ cm}^{-1}$ compared with samples (CON + CoNph) and (CON + CoNph + GC) without heating. After heating intensity of all the peaks have been increased, especially has been increased the absorption peak at 1040 cm^{-1} , corresponding to -C-OH group of atoms, that is the group which took place on this interaction.

Summarizing the research results of IR spectroscopy we can make the following conclusions:

- catalytic additive of ET and heating (CON + CoNph + GC) contributes to the destruction of hydrogen bonds presented in (CON + CoNph) and (CON + CoNph + GC);
- catalytic additive of ET promotes the formation of more polar molecules – micelles;
- interaction with complex formation occurred involving C-OH groups of the additives and reaction products.

The results of spectral studies of binary catalytic systems based on CoNph with the additives of different nature (alcohols and nitrogen-containing modifiers) can offer the following structural formula of the catalytic complexes (Fig. 2, 3):

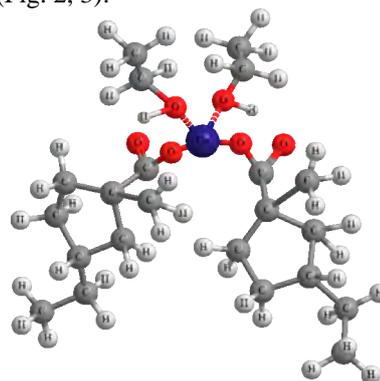


Fig. 2. Expected catalytic complex of cobalt naphthenate with ethanol

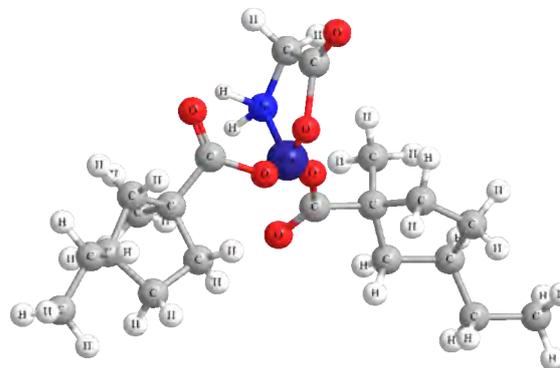


Fig. 3. Expected catalytic complex of cobalt naphthenate with glycine

Conclusion

The research of IR spectra indicates the creation and quantitative changes in the solutions that's confirms the assumption complexation involving all components of catalytic solutions.

References

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