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RESEARCH OF ACTION MECHANISM OF CATALYTIC SOLUTIONS IN THE OXIDIZATION PROCESS OF CYCLOHEXANE

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Abstract. Interbond between the efficiency of complex catalytic solutions action [cobalt naftenate–polyethyleneglicol–cyclohexanone] in the process of liquid-phase cyclohexane oxidization and complexation between the composite components of catalytic solution has been considered in the article.

Keywords: cyclohexane, oxidization, catalysis, complexation.

1. Introduction

The use of different nature modifiers allows to increase the efficiency of homogeneous catalyst action in the processes of hydrocarbons liquid-phase oxidation. However, the existing base of the given experimental investigations is not enough for determination of the action mechanism of these additions and prediction of their influence during their usage in different chemical processes.

The action effect of preliminary tested organic modifiers of homogeneous catalysts for cyclohexane oxidization process (chromoksan, crown-ethers, polyglicoles *etc.*) is connected with the complexation or ionic associates among the molecules of catalyst, co-catalyst and modifier. To confirm these suppositions spectral investigations of complex catalytic systems have been conducted.

2. Experimental

Complex catalytic solutions of cobalt naphthenate (CoNf) and polyethyleneglicol with the average molecular mass 2000 (PEG2000) in one of specified products of cyclohexane oxidization – cyclohexanone (CON) have been investigated [1, 2].

The concentration of CoNf in the tested solutions equaled to $5.0 \cdot 10^{-5}$ mol/l. Mass ratio of CoNf/PEG2000 was 1/1. The general concentration of the catalytic solution was equal to 5 mass %. The cyclohexane oxidation process was conducted in the laboratory reactor at $T = 418$ K and $P = 1.0$ MPa. Products composition was determined by titrimetric and chromatographic analyses.

The photocolorimetric analysis, IR- and UV-spectroscopy of the tested and comparative solutions – CoNf in CON and PEG2000 in CON – have been conducted.

3. Results and Discussion

The photocolorimetric analysis by side scattering method showed the presence of dispersion particles in the solution of pure polyethyleneglicol in CON. In solutions of pure CoNf and catalytic systems [CoNf–PEG2000–CON] no particles were discovered that allowed to conclude about bonds formation between cobalt naphthenate and polyethyleneglicol molecules.

The coloring change of prepared solutions [CoNf–PEG2000–CON] from violet to the greenish also points to complexation in catalytic systems.

This supposition is confirmed by the results of IR-spectroscopy of the tested solutions (Table1).

IR- spectroscopy of fresh and mature [CoNf+PEG2000+CON] solutions was conducted for more detailed study of catalytic solutions and for the possibility of coordination bonds formation: in Table 1 they are marked as $\tau = 0$ and $\tau = 1$ respectively. The period of $\tau = 1$ was 72 h.

The absorption band in the area of 3512 cm^{-1} is observed for $\tau = 0$, that is characteristic for OH-group, which do not form intramolecular bonds (hydrogen bonds). Thus at $\tau = 0$ in the interval of $1700\text{--}1720 \text{ cm}^{-1}$ the absorption band is observed responsible for the stretching vibrations of carbonyl group, regardless the functional group it belongs to (carbonyl group CON and CoNf) [3, 4].

Hydrogen intermolecular bonds are formed with time ($\tau = 1$). Wide intensive maximum absorption at $3200\text{--}3400 \text{ cm}^{-1}$ testifies to the participation of polyethyleneglicol hydroxylic group in inter- and intramolecular hydrogen bonds. Hydrogen bond can be formed between the carbonyl group CON and CoNf and hydroxylic group of PEG, thus the decrease of absorption band intensity proves it with time (Fig. 1).

Table 1

Results of IR-spectroscopy of catalytic and comparative solutions

| CoNf + CON | | PEG2000 + CON | | CoNf + PEG2000 + CON, $\tau = 0$ | | CoNf + PEG2000 + CON, $\tau = 1$ | |
|------------------------------------|--|------------------------------------|--|------------------------------------|--|------------------------------------|--|
| $\nu, \delta,$ cm^{-1} | group | $\nu, \delta,$ cm^{-1} | group | $\nu, \delta,$ cm^{-1} | group | $\nu, \delta,$ cm^{-1} | group |
| – | –C–O– | 1224 | –C–O– | 1220 | –C–O– | 1220 diminishes | –C–O– |
| 1564 | Co | – | – | 1568 | Co | 1564 increases | Co |
| 1732 | –C=O | 1712 | –C=O | 1728 | –C=O | 1728 diminishes | –C=O |
| 2948 | –CH ₃ , –CH ₂ – | 2944 | –CH ₃ , –CH ₂ – | 2912 | –CH ₃ , –CH ₂ – | 2864÷2936 diminishes | –CH ₃ , –CH ₂ – |
| – | – | 3512 | –OH | 3512 | –OH | 3512 diminishes | –OH |
| – | – | – | – | – | – | 3312 appears | –OH...H |

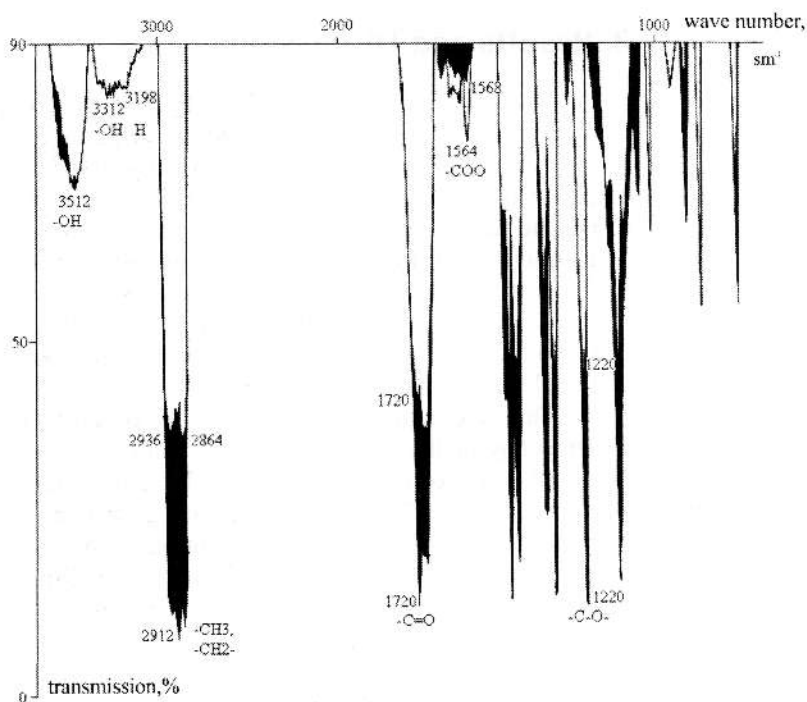


Fig. 1. IR-spectra of catalytic solutions [CoNf-PEG2000-CON]: $\tau = 0$ is a dark filling; $\tau = 1$ is a light filling

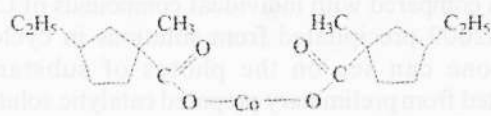
Chemism of this process can be foreseen in this way: the oxygen group of PEG is coordinated with the electron-seeking atom of Co, but the growth in time of OH-bonds capable to form hydrogen bond is due to the air oxygen oxidation of polyethyleneglycol methene group. The insignificant shift of C–H absorption bands testifies to it (Table 1, Fig. 2). Intensification of absorption band of carboxylated groups can be related with changing the coordination number of Co^{n+} ion and the number of ligands in the complex.

Formation of absorption band in the area of 3200 cm^{-1} testifies to the formation of intracomplex compounds bonds (Table 1, Fig. 2).

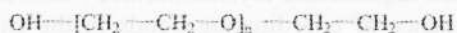
The results of IR-spectroscopy of the prepared solutions testify to the formation of OH...H-bonds, quantitative change of C=O and $-\text{CH}_3$, $-\text{CH}_2-$ bonds that is in its turn testifies to the formation of complex compound or ionic associate in a catalytic solution.

The peak shift of catalytic solutions absorption band on UV-spectrum ($\lambda = 510\text{--}560 \text{ nm}$) testifies to the complexation among the components of the catalytic system (Fig. 3).

These complexes are rather stable, the given pictures of the tested and comparative solutions made under "Zeiss Jenaval" microscope with the increase in 1000–2000 times testify to it.



cobalt naphthenate



polyethyleneglycol



cyclohexanone

Fig. 2. Types of chemical bonds and structure of catalytic solutions components

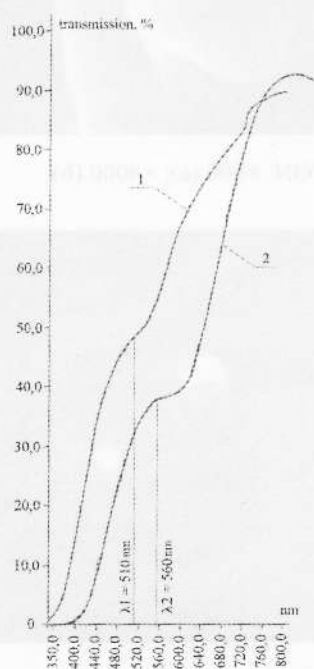


Fig. 3. UV-spectra of prepared catalytic solutions: CoNf+ CON (5 mass %) (1), CoNf+ PEG2000 + CON (5 mass %) (2)

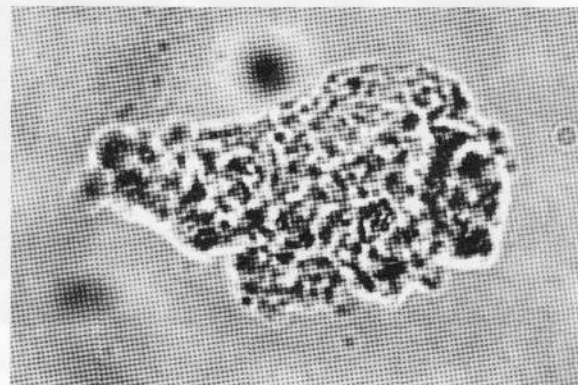
The general concentration of all tested solutions was 5 mass %, mass ratio between its components was 1:1 and cyclohexanone was used as a solvent.

As the comparative solutions there were the solution of individual CoNf and the solution of components mixture of CoNf and Crown-ether of di-benzo-18-Crown-6 (DBCR). Solution of [CoNf-DBCR-CON] was tested for comparing structural formations while applying compounds of different nature in catalytic solutions.

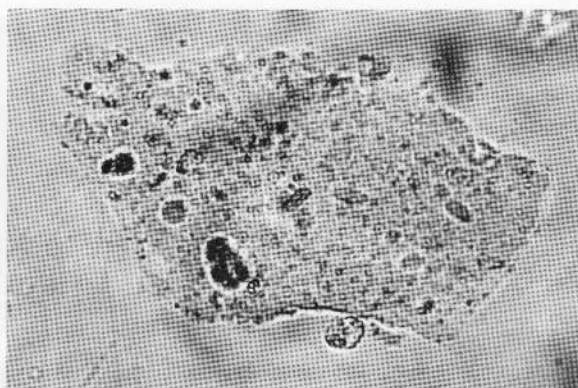
The obtained pictures testify to different structural formations in catalytic solutions (Fig. 4).



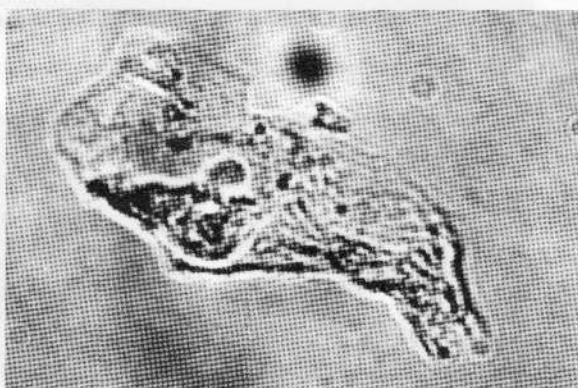
a



b



c



d

Fig. 4. Pictures of solutions of catalytic systems ($\times 1000$): CoNf+ CON* (a); CoNf+ PEG2000 + CON (b), CoNf+ PEG6000 + CON (c), CoNf+ DBCR + CON (d)

* - increasing $\times 2000$

There were also taken pictures of precipitated solutions using the method of scanning electronic microscopy on the "Tesla" device with the increase in 600 and 4000 times (Figs. 5–8).

To compare the precipitated from solutions compounds the substances precipitated from catalytic solution of [CoNf-PEG2000-CON] and the compounds precipitated from individual solutions of CoNf and PEG2000 in CON, were photographed.

As compared with individual compounds of CoNf and PEG2000 precipitated from solutions in cyclohexanone one can see on the photos of substances precipitated from preliminary prepared catalytic solutions the form and structure changes of particles coordination. In this case there are particles of PEG2000 co-catalyst on the cobalt naphthenate crystals surface which testifies to the presence of coordinating bonds in the catalytic system (Figs. 7, 8).

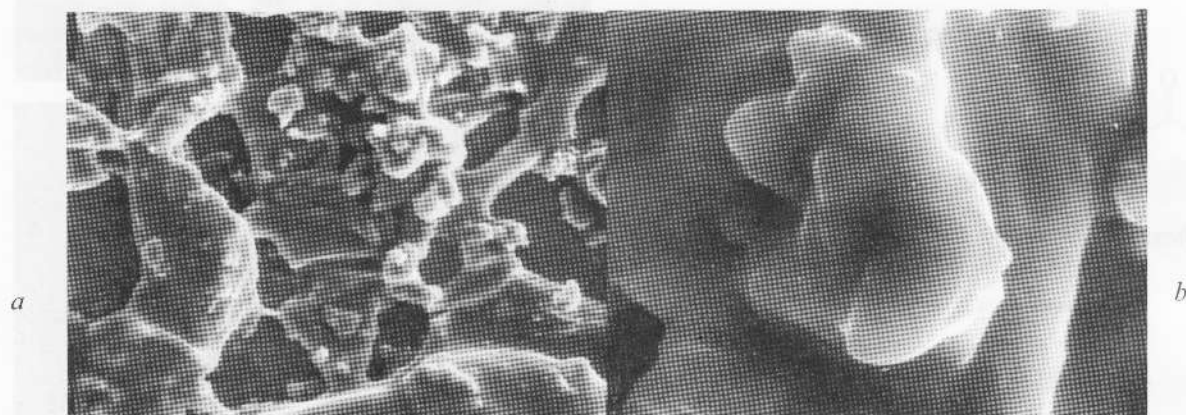


Fig. 5. Pictures of precipitated (5 mass %) solution of CoNf in CON: $\times 600$ (a); $\times 4000$ (b).



Fig. 6. Pictures of precipitated (5 mass %) solution of PEG2000 in CON: $\times 600$ (a), $\times 4000$ (b)



Fig. 7. Pictures of the precipitated (5 mass %) solution of [CoNf-PEG2000-CON], CoNf/PEG2000 = 1:1: $\times 600$ (a), $\times 4000$ (b)

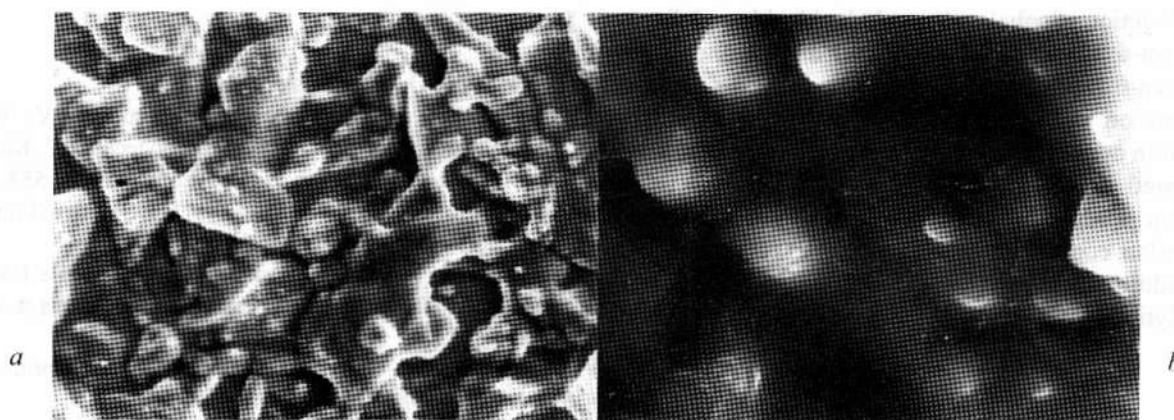


Fig. 8. Pictures of the precipitated (5 mass %) solution of [CoNf-PEG2000-CON], CoNf/PEG2000 = 5:1: $\times 600$ (a), $\times 4000$ (b)

The difference in precipitated substances structure is noted while changing the components ratio in the catalytic solution which testifies to different nature action of catalytic complex while its components ratio is varying (Figs. 7, 8).

Consequently, the conducted spectral analyses of catalytic solutions confirmed the formation of complexes or ionic associates with participation of all the solution compounds in the catalytic system.

Thus, the action effect of catalytic solutions can be explained by influencing the surface active compound in ionic associates.

To confirm the fact that the received effects are connected with complexation, the investigations of preliminary prepared Co^{2+} complexes while the cyclohexane oxidation process have been carried out.

For these investigations complexes in cobalt chloride composition and diazo-18-Crown-6 ($[\text{CoCl}_2 + \text{CE}]$) as well as cobalt acetate and diazo-18-Crown-6 ($[\text{Co}(\text{OAC})_2 + \text{CE}]$) have been used.

Crown-ether (CE) was used as addition since Crown-ether is an individual compound, unlike polyglycoles, the molecular mass of which changes. Coordinating and surface active properties of Crown-ethers and polyglycoles are similar [5].

Table 2

Effect of complex catalysts nature on cyclohexane catalytic oxidation
[CoNf] = $5 \cdot 10^{-5}$ – $5 \cdot 10^{-4}$ mol/l, T = 418 K, P = 1 MPa

| Catalyst | K, % | Selectivity, % | | | | | | [COL]/[CON] |
|---|------|-------------------|-----------------|-----------------|------|------|------------------|-------------|
| | | CGHP ¹ | AC ² | ET ³ | COL | CON | SPP ⁴ | |
| CoNf | 2.7 | 11.1 | 11.5 | 22.6 | 36.1 | 18.7 | 73.4 | 1.94 |
| CoNf + PEG2000 + CON | 2.4 | 3.7 | 9.5 | 5.3 | 47.2 | 34.3 | 87.0 | 1.38 |
| $[\text{Co}(\text{OAC})_2 + \text{CE}]$ | 2.8 | 6.2 | 8.8 | 7.1 | 43.1 | 34.8 | 86.5 | 1.24 |
| $[\text{CoCl}_2 + \text{CE}]$ | 1.6 | 13.0 | 6.4 | 13.1 | 41.5 | 26.1 | 84.9 | 1.59 |

Note: ¹cyclohexyl hydroperoxide, ²acids, ³ethers, ⁴desired products

The qualitative influence of the tested complex catalysts on the basis of Co^{2+} salts is identical to the action of catalytic solutions of CoNf and PEG in cyclohexanone (Table 2).

Using both complex formations of cobalt and catalytic solutions of CoNf and PEG in cyclohexanone the selectivity to acids, CGHP and ethers considerably

decreases while the selectivity to desired products (COL and CON) increases. Ratio [COL]/[CON] shifts to the CON. The presence of inorganic CoCl_2 salt in the complex with CE does not allow to decrease the selectivity to CGHP.

On the basis of conducted investigations it is possible to conclude about the identical mechanism of

catalytic action of cobalt salts—cobalt chloride and diazo-18-Crown-6 ($[\text{CoCl}_2+\text{CE}]$) and cobalt acetate and diazo-18-Crown-6 ($[\text{Co}(\text{OAc})_2+\text{CE}]$) complexes as well as solutions on the basis of CoNf and surface active addition in cyclohexanone since the influence of above-mentioned catalytic systems on the selectivity of oxidation products is similar and does not depend on preparation conditions of the catalytic system, which is the additional confirmation of complexes formation in catalytic solutions on the basis of CoNf and PEG in CON.

4. Conclusions

Thus, on the basis of spectral investigations and model experiments it was concluded that the effective catalytic action of complex catalytic solutions is connected with intermediate complexation between the components of the catalytic system. The obtained results allow to forecast the effect of organic additions on homogeneous catalysts depending on modifier nature which simplifies planning and conducting of experimental investigations for creation of effective catalytic systems for industrial oxidation processes.

References

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ДОСЛІДЖЕННЯ МЕХАНІЗМУ ДІЇ СКЛАДНИХ КАТАЛІТИЧНИХ РОЗЧИНІВ У ПРОЦЕСІ ОКИСНЕННЯ ЦИКЛОГЕКСАНУ

Анотація. У статті розглянуто взаємозв'язок між ефективністю дії складних каталітичних розчинів [нафтенат кобальту—поліетиленгліколь—циклогексанон] у процесі рідинно-фазного окиснення циклогексану та комплексоутворенням між складовими компонентами каталітичних розчинів.

Ключові слова: циклогексан, окиснення, каталіз, комплексоутворення.