

Catalytic Cyclohexane Oxidation In The Presence Of Alcohols Of Different Nature

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Abstract – *Quantitative and qualitative influence of binary catalytic systems [cobalt naphthenate – alcohol] in liquid-phase homogeneous-catalytic oxidation of cyclohexane was considered.*

Key words – cyclohexane, oxidation, catalysis, catalytic systems

I. Introduction

One of the main directions in regulating the activity and selectivity of homogeneous-catalytic carbons oxidation is the use of organic compounds of different nature. The common property of these compounds is the ability to create interim complexes with the catalyst, thus enabling them to influence the reaction process [1]. These interim complexes include not only the metal salts of varying basicity with an organic component, but also oxygen-rich compounds, which are created in the oxidation process [2]. As suggested by previous research, alcohols created during oxidation play an important role in the existence of these complexes [3]. With this in mind, it made sense to explore the previously-created catalytic compounds, which include alcohols of different nature. We analyzed the influence of binary catalytic systems on the process of homogenous-catalytic oxidation of cyclohexane (CYH). These catalytic systems were comprised of cobalt naphthenate (CoNph) and alcohols of different nature – glycerin (GL), ethylene glycol (EG), ethanol (ET), propanol (PR) and pentanol (PN).

II. Experimental part

Cyclohexane oxidation was performed at the temperature of 413 K and pressure P=1,0 MPa, with the presence of binary catalytic systems. These conditions are close to the ones which are used in the industrial process. Industrial oxygen was used as the oxidant [4].

The research was performed on an experimental autoclaved set up with electrical heating of the reactors shell, the description of which is identical to the one used in the work [5]. Stable temperature conditions were maintained using silicon oil, contained in the reactors shell.

Samples were taken using containers pre-processed with isopropyl alcohol. It was done to homogenize the samples and dissolve the adipic acid, which is created in

substantial quantities as the cyclohexane conversion progresses. Product composition was analyzed using titrimetric and chromatographic approaches.

III. Results and discussion

The most important component of analyzing the obtained experimental data is to make sure the process indicators for the cyclohexane conversion are close to 2 % and 4% [6]. These are critical conversion values at which (2%) it is possible to observe the effect of using a process catalyst, and which (4%) are the closest to the ones used in industrial cyclohexane oxidation. The results are compared to the data obtained when oxidizing CYH with an individual industrial catalyst – CoNph (table 1).

After performing research of cyclohexane oxidation with the presence of binary catalytic systems which contain glycerin and ethylene glycol, we arrive at the conclusion that using alcohols in the oxidation process causes a decrease in selectivity according to COL and CON. This result is consistent for the initial stages of oxidation ($X \sim 2\%$) and also for the more advanced stages ($X \sim 4\%$), when compared to CoNph. However, supplements have a substantial influence on the [COL/CON] correlation in the oxidate. All the cases exhibit an increase in the correlation of the COL/CON, and the largest deviation toward alcohols accumulation takes place with low values of conversion X, when EG – [COL/CON]=11,29. However, for advanced oxidation, the highest value of [COL/CON] = 1,72 can be reached using GL. The addition of alcohols had a substantial influence on the percentage of ethers in the final product at both oxidation stages. The use of EG produced an increase in the ester selectivity, which was 54% with $X \sim 2\%$ and close to 17% with $X \sim 4\%$. During the production process this lets us to increase the COL selectivity, thus further shifting the [COL/CON] correlation. Also, the addition of EG during advanced oxidation increases the content of acids by 2,4%, the majority of which is represented by the adipic acid. This aspect could be used to produce adipic acid.

It became reasonable to determine the influence of the supplement concentration on the oxidation process. We performed research of the process with varying correlations between the supplements and CoNph. The content of CoNph in the reactionary mixture remained constant ($CCoNph = 5,0 \times 10^{-4}$ mole/l). CYH conversion dependencies with different alcohol supplement correlations were developed (Fig. 1,2).

Based on the graphic dependencies, it is evident that adding multi-atom supplements to CoNph inhibits the process at the initial oxidation stages. However, once sufficient quantities of oxygen-rich compounds are accumulated, the reaction speeds up. The comparison of product accumulation speeds presents a self-evident example (tab. 2.).

Experimental data shows an increase of v_{av} and v_x (v_x represents the speed of product accumulation at 3600 s from the moment the reaction was carried out) in all the cases where alcohol supplements were used, as compared to CoNph. The highest average speed values were

TABLE 1

OXIDATION INDICATORS OF CYCLOHEXANE WITH CONVERSION VALUES AT $X \sim 2\%$, $X \sim 4\%$
 $T = 413\text{ K}$, $P = 1,0\text{ MPA}$, $C_{\text{CoNph}} = 5,0 \times 10^{-4}\text{ MOLE/L}$

Catalyst	S(CHP ¹), %	S(A ²), %	S(ET ³), %	S(COL ⁴), %	S(CON ⁵), %	[COL/CON]
Conversion $X \sim 2\%$						
CoNph	7,14	6,73	0,00	60,14	25,99	2,31
CoNph + GL	4,09	3,37	30,67	47,24	14,62	3,23
CoNph + EG	5,45	5,49	54,47	31,77	2,81	11,29
Conversion $X \sim 4\%$						
CoNph	1,77	6,04	10,63	47,25	34,32	1,38
CoNph + GL	2,84	6,03	24,38	42,17	24,58	1,72
CoNph + EG	2,20	8,46	27,45	37,70	24,19	1,56

Note: ¹ cyclohexyl hydroperoxide; ² acids, ³ ethers, ⁴ cyclohexanol, cyclohexanone

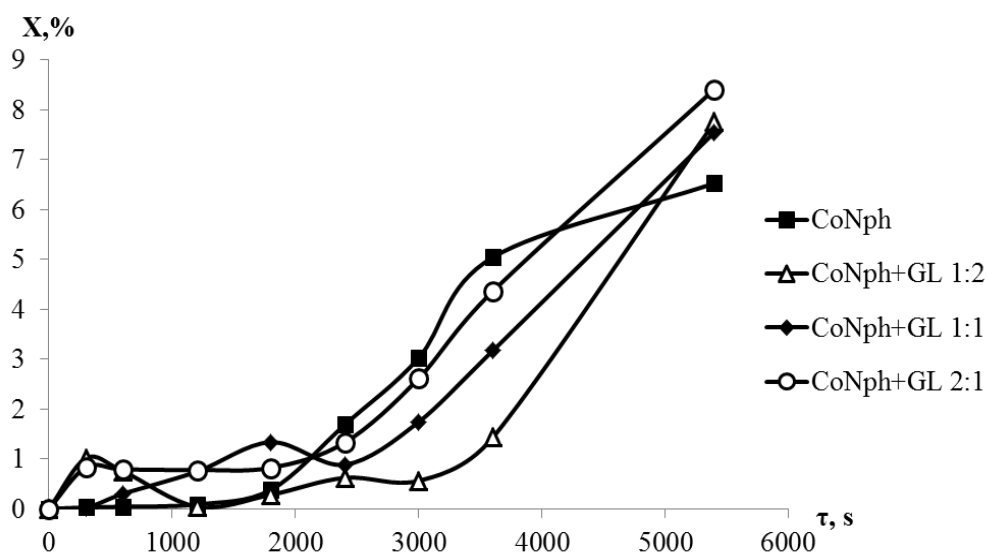


Fig. 1 The dependence of the CYH conversion degree from the duration of oxidation with the use of GL supplement.

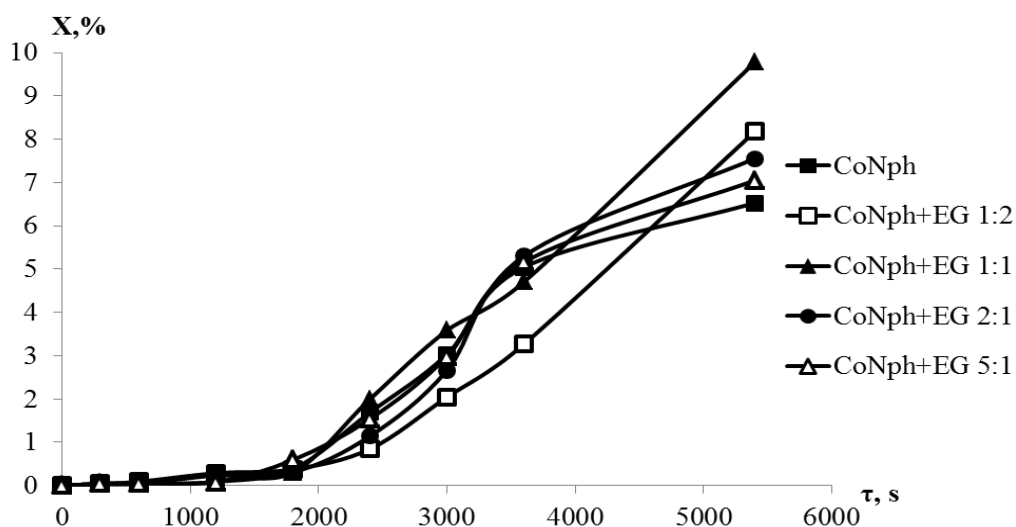


Figure 2. The dependence of the CYH conversion degree from the duration of oxidation with the use of EG supplement.

TABLE 2

ACCUMULATION SPEED VALUES FOR PRODUCTS OF BINARY CATALYTIC SYSTEMS

Catalyst	v_{av} , $\times 10^{-4}$ mole/s	v_x , $\times 10^{-4}$ mole/s	Catalyst	v_{av} , $\times 10^{-4}$ mole/s	v_x , $\times 10^{-4}$ mole/s
CoNph	1,12	0,764	CoNph + EG 1:2	1,4	2,53
CoNph + GL 1:2	1,33	3,25	CoNph + EG 1:1	1,68	2,61
CoNph + GL 1:1	1,29	2,25	CoNph + EG 2:1	1,29	1,16
CoNph + GL 2:1	1,44	2,09	CoNph + EG 5:1	1,21	0,97

Note: v_{av} – the average speed of product accumulation, v_x – the speed of product accumulation of advanced oxidation

TABLE 3

 OXIDATION INDICATORS OF CYCLOHEXANE WITH CONVERSION VALUES AT $X \sim 2\%$, $X \sim 4\%$
 $T = 413\text{ K}$, $P = 1,0\text{ MPA}$, $C_{\text{CoNph}} = 5,0 \times 10^{-4}\text{ MOLE/L}$

Catalyst	S(CHP), %	S(A), %	S(ET), %	S(COL), %	S(CON), %	[COL/CON]
Conversion $X \sim 2\%$						
CoNph	7,14	6,73	0,00	60,14	25,99	2,31
CoNph + ET	86,67	13,33	0,00	0,00	0,00	—
CoNph + PR	80,00	20,00	0,00	0,00	0,00	—
CoNph + PN	6,85	10,96	82,19	0,00	0,00	—
Conversion $X \sim 4\%$						
CoNph	1,77	6,04	10,63	47,25	34,32	1,38
CoNph + ET	11,39	1,95	0,00	69,26	17,40	3,98
CoNph + PR	7,19	1,92	5,75	69,49	15,65	4,44
CoNph + PN	1,18	2,36	7,08	62,86	26,52	2,37

TABLE 4

 OXIDATION INDICATORS OF CYCLOHEXANE WITH CONVERSION VALUES AT $X \sim 4\%$
 $T = 413\text{ K}$, $P = 1,0\text{ MPA}$, $C_{\text{CoNph}} = 5,0 \times 10^{-4}\text{ MOLE/L}$

Catalyst	S(CHP), %	S(A), %	S(ET), %	S(COL), %	S(CON), %	[COL/CON]
Conversion $X \sim 4\%$						
CoNph	1,77	6,04	10,63	47,25	34,32	1,38
CoNph + ET	11,39	1,95	0,00	69,26	17,40	3,98
CoNph + EG	2,20	8,46	27,45	37,70	24,19	1,56
CoNph + PR	7,19	1,92	5,75	69,49	15,65	4,44
CoNph + GL	2,84	6,03	24,38	42,17	24,58	1,72

achieved using a 1:1 CoNph/EG proportion – $1,68 \times 10^{-4}$ mole/s, and the speed of advanced oxidation with CoNph + GL 1:2 – $3,25 \times 10^{-4}$ mole/s. It is worth noting that increasing the share of the supplement increases the speed of advanced oxidation products accumulation, and this property should be explored further.

Similar research was also performed for catalytic systems which contained single-atom alcohols. Process indicators with conversion values close to 2% and 4% were explored. The following CoNph supplements were analyzed – ethanol, propanol and pentanol. Experimental data of the study is further compared with CoNph, and multi-atom alcohol supplements (table 3).

Obtained data indicates that the use of single-atom alcohols leads to the exclusion of COL and CON from the products of the reaction, when the conversion degree of the initial substance is close to 2%. However,

supplements have a substantial influence in the process of advanced oxidation, as on the value of selectivity for COL and CON, and also on the magnitude of their correlation. Catalytic systems which contained single-atom alcohols are characterized by an increase in selectivity of COL (the largest values can be achieved by using ET – 69.26% and PR – 69.49%) and a decrease of CON, which in turn leads to an increase of the [COL/CON] correlation, the maximum value of which is 4,44 with the addition of PR. Selectivity by acids and ethers substantially decreases in all the experiments with the use of single-atom alcohols. The lowest selectivity indicators with acids were caused by supplements PR – 1,92% and ET – 1,95, which are 3 times lower in comparison with CoNph and multi-atom supplements. The use of ET allowed to maximally reduce the selectivity according to ET. It is worth to note the increase of selectivity for CHP with the presence of ET

and PR supplements, the maximum value of which can be achieved with ET – 11.39%.

The provided data indicates that the increase in a spirits molecular mass causes a decrease in the CHP content and an increase in the number of esters in the oxidate. This typical dependence is not observed for any other indicators. In addition to the length of the chain, the basicity of the alcohols can also have a substantial influence on the product correlation (table 4).

When comparing the use of EG and ET supplements, we can see that the use of ET allows to increase the outputs of CHP, COL, and also to increase the correlation value of [COL/CON] and accordingly reduce the content of acids, ethers, and CON. The use of PR and GL produces an identical qualitative influence on the product accumulation in the oxide, with their different quantitative correlations.

From a technological point of view the best results were achieved with the use of single-atom alcohols. The highest selectivity by COL (69,49%) and the maximum value of [COL/CON] correlation (4,44) can be reached by using the PR supplement.

Conclusion

The use of binary catalytic systems which contain single-atom alcohols causes the increase of selectivity for COL and a decrease for CON. They have substantial influence on the quantity of CHP, acids and ethers, and on the correlation of [COL/CON]. Specifically, adding PR (when X ~ 4 %) allows to reach maximum selectivity at COL (69,49%) and increase the values of [COL/CON] by 3,2 times as compared with individual CoNph. Adding ET (when X ~ 4 %) allows to decrease acidic concentration to 1,95% and to maximally reduce the percentage of esters in the oxide. We determined the dependence for reaction speed of liquid phase oxidation from the nature of the supplements and correlation between the components. It was established that the most positive influence on the content of products in the oxidate can be achieved by adding PR in equal proportions with CoNph – 1:1.

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