

Cyclohexane oxidation in the presence of alcohol containing catalytic systems

O. Suprun, V. Reutskiy, O. Ivashchuk, S. Mudriy

*National University "Lviv Polytechnic",
12, S. Bandera Str., 79013 Lviv, Ukraine,
Tel.: (093) 639-81-87, E-mail: terick-zol@rambler.ru*

Work is devoted to study of the effect of two- and three-component catalytic systems of cobalt naphthenate at liquid-phase homogeneous catalytic oxidation of cyclohexane. The dependences of the process speed and quality of products accumulation from the composition of the catalytic system were determined. Article also contains comparison of impact on process depending on different structure of catalyst.

Introduction

Processes of catalytic hydrocarbons oxidation are widely used in industry of organic synthesis. One of such processes is homogeneous catalytic oxidation of cyclohexane (CH) to cyclohexanone (CHN) and cyclohexanol (CHL), which is conducted in presence of metals of variable valency (MVV). Organic modifiers of different nature are used for improving of process indexes (conversion and selectivity) [1] and their effect appears after accumulation of oxidation products in the reaction mixture.

Previous studies have shown that the addition of alcohols to industrial cobalt naphthenate catalyst (NC) has positive effect on the oxidation of CH. Quantitative measurements of this effect depends on the structure of alcohol (chain length and the number of OH-groups) [2]. It was found that from a technological point of view, the best results are observed with monoatomic alcohols [2]. With this in mind, organic modifiers of different nature combined

with pre-created binary catalytic system NC + ethanol (ET) has become the object of research. Influence of three-component catalytic systems consisting from [NC+ET] and organic additives – polyethylene glycol (PEG with $M \sim 400$), glycine (GL) and aminesulfonic acid (AS) at catalytic CH oxidation were analyzed.

Experimental part

Investigation of the influence of catalytic systems for homogeneous catalytic oxidation of CH was carried out in a reactor of bubbling type (Fig. 1) under temperature $T = 413$ K and pressure $P = 10$ atm. Technical oxygen was used as oxidant. The concentration of the catalytic system was chosen with reference to previous studies where was found optimum catalyst content – 5×10^{-4} mol/l [3].

Samples were taken in containers with previously amended isopropyl alcohol, for homogenization of samples and dissolution of adipic acid, which is formed in large numbers with increase of cyclohexane conversion degree.

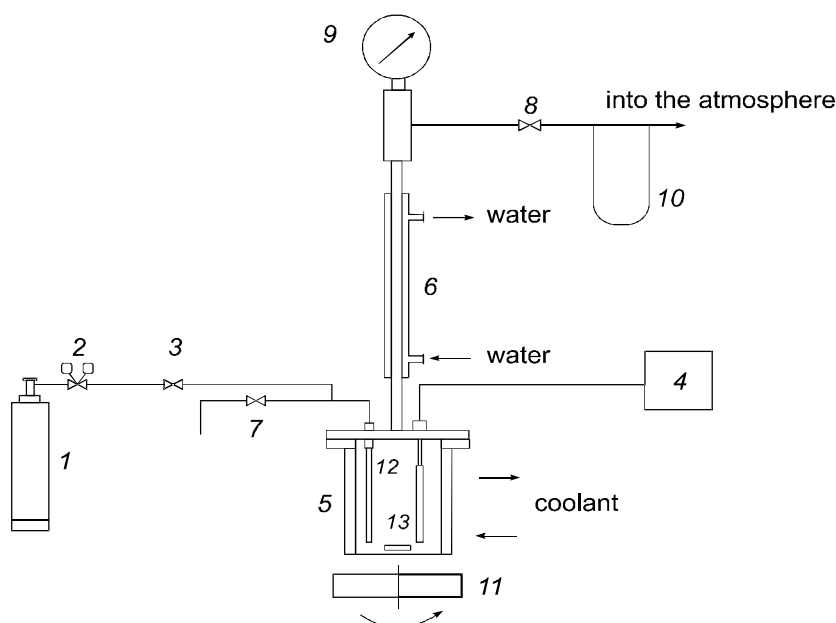


Figure 1. Autoclave plant for cyclohexane oxidation: 1 – oxygen cylinder, 2 – reducer, 3, 7, 8 – valves, 4 – control equipment, 5 – reactor for cyclohexane oxidation, 6 – shell-and-tube heat exchanger, 9 – pressure gauge, 10 – differential pressure gauge for the oxygen cost measuring, 11 – magnetic mixer, 12 – capillary for oxygen, 13 – thermocouple.

Table 1. Indicators of cyclohexane oxidation at conversion value $X = 2\%$, $X = 4\%$, $T = 413\text{ K}$, $P = 1,0\text{ MPa}$, $C_{\text{NC}} = 5,0 \cdot 10^{-4}\text{ mol/l}$

Catalyst	S(HPCH*), %	S(A), %	S(ES), %	S(CHL), %	S(CHN), %	[CHL/CHN]	W, mol/l·s
Conversion $X \sim 2\%$							
NC	22,11	15,84	0,00	36,70	25,35	1,45	$1,11 \cdot 10^{-4}$
[NC+ET]	23,77	19,02	0,00	36,43	20,78	1,75	$1,12 \cdot 10^{-4}$
Conversion $X \sim 4\%$							
NC	10,32	22,01	5,90	37,26	24,52	1,52	$2,11 \cdot 10^{-4}$
[NC+ET]	10,82	21,85	0,00	42,42	24,90	1,70	$5,89 \cdot 10^{-4}$

*: W – speed of CH consumption mol/(l·s)

Concentration of following substances in oxydate: hydroperoxide of cyclohexyle (HPCH), dicarboxylic acids (A) (in terms of adipic acid) and esters (ES) (on dicyclohexyl adypinate was determined by titration method of analysis. The content of cyclohexanol (CHL) and cyclohexanone (CHN) were determined chromatographically.

Results and analysis

During analysis of the experimental data we were interested primarily in the process indicators under CH conversion (X) close to 2 % and 4 %. $X = 2\%$ was chosen due to the fact that this critical conversion, in which it is possible to observe the practical effect of the catalytic process; value of $X = 4\%$ is close to the parameters of the industrial process of cyclohexane oxidation. The results of studies on the effect of three-component catalytic systems were compared with the industrial catalyst NC (Table 1).

As can be seen from the data, the use of ethanol as part of a binary catalyst system [NC + ET] leads to an increase in selectivity for CHL (as $X \sim 4\%$), and to increase of ratio value CHL / CHN at both stages of oxidation. The binary catalyst system significantly increases the rate of CH consumption in the second stage of the process. Also the presence of [NC + ET] excludes esters from cyclohexane oxidation products and reduces the acid content in oxydate.

Effects of ethanol usage in the ternary catalytic systems depend on the properties of organic additives (Table 2).

The use of ethanol as part of three-component systems is significantly different from the effect on individual CN, – selectivity for acids increases, selectivity for esters and alcohols decreases, the rate of oxidation decreases as well. More quantitative effect was obtained during usage of etha-

nol in the catalytic system containing glycine.

Discussion

Obtained data showed that the use of alcohol (for example ethanol) as additive to the homogeneous catalysts leads to changes in both – their activity and selectivity in their action. Various qualitative effect of ethanol on individual CN and binary catalytic systems suggests that alcohol not only affects the intermediate radicals formed during oxidation, but also takes part in the formation of the actual catalytic complexes.

Previous studies have shown that the effect of organic modifiers is connected primarily to their participation in the creation of catalytic complexes [4]. This correlates with the literature data and the ability to create complexes with metals [5]. For glycine example, the structure of the catalytic complex might look like this (Figure 2, 3).

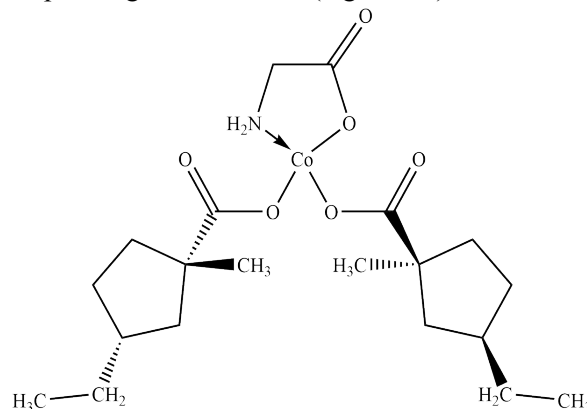


Figure 2. Predicted intermediate complex NC + GL

Table 2. Indicators of cyclohexane oxidation in presence of binary and ternary catalytic systems at conversion value $X = 2\%$, $X = 4\%$ ($T = 413\text{ K}$, $P = 1,0\text{ MPa}$, $C_{\text{NC}} = 5,0 \cdot 10^{-4}\text{ mol/l}$)

Catalyst	S(HPCH*), %	S(A), %	S(ES), %	S(CHL), %	S(CHN), %	[CHL/CHN]	W, mol/(l·s)
Conversion $X \sim 4\%$							
NC + AS	9,94	6,21	7,45	48,88	27,52	1,78	$3,03 \cdot 10^{-4}$
[NC+ET]+AS	9,03	22,47	6,02	34,43	28,05	1,23	$2,09 \cdot 10^{-4}$
NC + GL	11,11	4,17	16,67	46,17	21,89	2,11	$5,42 \cdot 10^{-4}$
[NC+ET]+GL	11,57	24,54	6,94	32,22	24,72	1,30	$3,04 \cdot 10^{-4}$

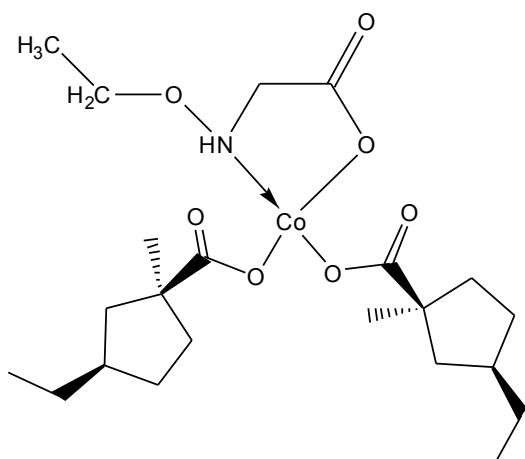


Figure 3. Predicted intermediate complex [NC + ET + GL]

Effectiveness of homogeneous catalysts is related to the properties of the metal cation. Glycine and ethanol coming into the catalytic complexes alter the electron density at the metal cations, which affects both the activity and the stability of the intermediate catalytic complexes.

Conclusion

Studies have found different qualitative and quantitative impact of ethanol additives on individual cobalt naphthenate and binary catalytic systems, due to the different structure and thus the catalytic activity of intermediate complexes.

1. Іващук О.С., *Інтенсифікація каталітичного окиснення циклогексану*, Вісник НУ „Львівська політехніка”, Хімія, технологія речовин та їх застосування, 726, 2012, 172–176.

2. Супрун О.О., Реутський В.В., Іващук О.С., Мудрий С.О., *Каталітичне окиснення циклогексану в присутності спиртів різної природи*, Східноєвропейський журнал передових технологій, Харків, 3/6 (69), 2014, 27–31.

3. Іващук О.С., Мудрий С.О., Мельник І.Р., Реутський В.В., *Окиснення циклогексану в присутності розчинів бінарних каталітичних систем*, Вопросы химии и химической технологии, Днепропетровск, 2008, (1), 63–66.

4. Mudryy S., Reutskyy V., Ivashchuk O., Suprun O., *Effect of nitrogen- and oxygen-containing additives on the efficiency of the catalytic oxidation of cyclohexane*, Proceedings of the 3-rd International Conference of Young Scientists, “Chemistry and chemical technology” CCT-2013, November 21–23, 2013, Lviv, Ukraine, P. 20.

5. Помогайло Л.Д., Уфлянд И.Е., *Макромолекулярные металлохелаты*, Москва, Химия, 1991.

Received to the editors 23.09.2014.

Окиснення циклогексану в присутності спиртовмісних каталітичних систем

О.О. Супрун, В.В. Реутський, О.С. Иващук, С.О. Мудрий

*Національний університет "Львівська політехніка",
Україна, 79013 Львів, вул. С. Бандери, 12,
Тел.: (093) 639-81-87, E-mail: terick-zol@rambler.ru*

Розглянуто вплив двох- та трьохкомпонентних каталітичних систем на основі нафтенату кобальту на рідиннофазне гомогенно-каталітичне окиснення циклогексану. Встановлено залежності швидкості та якості накопичення продуктів від складу каталітичної системи та виконано порівняння впливу каталізаторів різної структури.

Окисление циклогексана в присутствии спиртсодержащих каталитических систем

А.А. Супрун, В.В. Реутский, О.С. Иващук, С.О. Мудрый

*Национальный университет "Львовская политехника",
Украина, 79013 Львов, ул. С. Бандеры, 12,
Тел.: (093) 639-81-87, E-mail: terick-zol@rambler.ru*

Рассмотрено влияние двух- и трехкомпонентных каталитических систем на основе нафтената кобальта на жидкофазное гомогенно-каталитическое окисление циклогексана. Установлены закономерности скорости и качества накопления продуктов от состава каталитической системы, а также выполнено сравнение влияния катализаторов разной структуры.