

The influence of the coordination properties of metals on the activity of binary catalysts for the oxidation of cyclohexane

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This paper proposes the possibility of creating an efficient binary catalytic system for the industrial oxidation process of cyclohexane based on a compound of a metal of variable valence and salt of perfluorinated sulfonic acid. Two-component binary mixtures of the main component and additive were used for the study.

Keywords – oxidation, cyclohexane, binary catalytic system, conversion of raw material, selectivity of aim products.

Introduction

Oxidation processes are one of the groups that play a key role in the modern chemical industry. Oxidation processes usually are carried out under industrial conditions in the gas phase using heterogeneous catalysts and in the liquid phase using homogeneous catalysts.

The catalyst in any industrial process can be used under the condition that it meets the requirements for activity and selectivity. The cost of raw materials and energy for its production, environmental protection, and utilization of production waste plays a significant role.

Studies of single-component catalysts in oxidation processes have shown that while affecting the ratio of formed products and oxidation rate they can not increase the yield of target products, as well as increase the oxidation rate of hydrocarbons compared to industrial catalysts. One way to solve this problem is to develop efficient binary catalytic systems, which are often more efficient than single-component catalysts.

This work's main aim was to define the dependencies of efficiency of organic modifiers from the nature of metal in the main catalytic salt. Defining those dependencies will allow us to create a binary catalytic system on the basis of variable valency metal compound [CVVM] and salt of perfluoric sulfur acid [SPSA], with activity and selectivity higher than for industrial catalysts for the oxidation process.

Page Setup

At the first stage of research, the combined effect of various salts of metals of variable valence in the binary catalyst system on the oxidation of cyclohexane was determined. Cobalt and manganese naphthenate, as well as copper, nickel, and cerium stearates, were used for this purpose. As an additive used one salt of perfluorinated sulfonic acid - chromoxane. Two groups of experiments were performed: in the presence of individual SVVM and under the action of binary mixtures with a ratio of components [SVVM] / [chromoxan] as 10/1.

The results of the experiments showed (Table 1) that only the presence of a binary catalyst system based on cobalt naphthenate or cerium stearate with the addition of chromoxane causes an increase in the oxidation rate of cyclohexane. Suppose we consider the change in selectivity for the

target products in the presence of SVVM and chromoxane. In that case, only binary catalyst systems based on cobalt and cerium salts lead to an increase in this parameter. The process of oxidation of CH in the presence of cerium stearate with the addition of chromoxane significantly increases the selectivity of the formation of CHH and acids, slightly increases the selectivity of the formation of COL and CON (18.8 and 13.7%, respectively), and the formation of esters decreases compared to oxidation on pure cerium stearate. It should be noted that the increase in hydroperoxide content in this case due to the explosiveness of this product impairs the safety of the process.

Table 1

Composition of cyclohexane oxidation products in the presence of chromoxane and salts of various metals of variable valence

T = 413 K, P = 1 MPa, [cat.] = $5 \cdot 10^{-4}$ mol / l, [SVVM] / [Chromoxane] = 10/1

Catalyst		τ , min	Selectivity, % mol.					Conversion, %mol.
Main comp.	Additive		CHH	Acids	Ethers	CON	COL	
CoNaf ₂	-	30	11,2	13,8	2,0	24,2	49,8	4,6
CoNaf ₂	Chromoxane	30	5,5	9,7	8,1	32,5	44,2	5,4
MnNaf ₂	-	60	27,6	5,4	10,1	21,7	35,2	4,0
MnNaf ₂	Chromoxane	80	36,5	9,4	13,2	15,7	25,2	3,4
CuSt ₂	-	90	43,0	6,5	23,3	13,0	14,2	4,2
CuSt ₂	Chromoxane	90	52,3	5,2	18,1	13,9	10,5	3,1
NiSt ₂	-	120	21,7	13,4	19,8	19,5	25,6	4,4
NiSt ₂	Chromoxane	120	46,0	7,8	11,2	15,5	19,5	4,2
CeSt ₃	-	65	28,4	4,0	44,2	9,9	13,5	4,0
CeSt ₃	Chromoxane	90	36,6	11,1	19,8	13,7	18,8	4,5

In the process of oxidation of CH under the influence of cobalt naphthenate and chromoxane decreases the selectivity of the formation of hydroperoxide and acids, increases the selectivity of the formation of the desired CHH and CON, as well as undesirable esters compared to oxidation without chromoxane. For this reason, this binary catalyst system may be of practical interest: cobalt naphthenate - chromoxane. Thus, cobalt is a necessary component of catalytic systems for the oxidation of cyclohexane.

Structural comparison of the “ligand” part of the catalytic system - chromoxane - with other SPSA shows that chromoxane is a “medium”, in size, compound, therefore, we cannot explain its influence by the possibility of more “loose” coordination around complex creating metal, or by the possibility of increase (or decrease) of the numbers of coordinated ligands. Also, it is worth mentioning that it is not the only compound containing potassium, so the solubility of SPSA as well can't explain such effectiveness in the oxidation process.

The next step of our research was the investigation of the characteristics of the individual metals that are used in the formation of a catalytic system. The main characteristics of metals are presented in Table 2.

As can be seen from Table 2. all characteristics of cobalt, in comparison with similar variable valency metals, are in the “middle” range. The influence of cobalt can not be explained by the size of the ion, as it is neither the biggest nor the smallest from the researched. As well as electronegativity doesn't play part in the efficiency of cobalt as a catalyst. Both - more electronegative and less electronegative metals - showed weaker results than cobalt. In terms of coordination numbers - the ability to form complex compounds - cobalt as well demonstrates characteristics similar to other researched metals.

In the case of CH oxidation process, we can't explain the difference in the impact of different metals by the structure of the surface of researched metals, as it is not a heterogeneous but homogeneous catalytic process.

Table 2

Main characteristics of the metals of variable valencies, used for the research

Element	Group	Family	Coordination number	Ion radius, pm	E potential, V	Electronegativity
Co	4 VIII B	d	4;6	63 (+3); 72(+2)	-0,277	1,88
Mn	4 VII B	d	4	46(+7); 80(+2)	-1,18	1,55
Cu	4 I B	d	6	73(+2);77(+1)	0,337	1,9
Ni	4 VIII B	d	4;6	69(+2)	-0,25	1,91
Ce	6 lant.	f	6	92(+4);103(+3)	-2,34	1,08

Our hypothesis for the mechanism of the catalytic reaction is that cobalt naphthenate forms a highly reactive, short-term, complex with SPSA and reaction media that have relatively low energy of activation and under reaction conditions transforms into the aim products, mainly CHH. This hypothesis is also proven by the higher percentage of ethers found in the products of the reaction. However, very specific conditions of creation and high instability of the catalytic complexes don't allow us to identify their presence and exact composition by any accessible to us methods of analysis. Developing new methods of identification of such catalytic complexes in the reaction media under high reaction conditions becomes very relevant and can help to find new highly effective catalytic systems for industrial processes.

Conclusions

Conducted experiments and research on the influence of organic modifiers of different natures on organic catalysts with different compositions for cyclohexane oxidation proved that the most efficient catalysts are based on the cobalt naphthenate. The mechanism of the catalytic reaction can be explained by the fact that cobalt naphthenate forms a highly reactive, short-lived, complex with SPSA and the reaction medium, which has relatively low activation energy and is converted to the target products, mainly cyclohexyl hydroperoxide, under the reaction conditions.

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