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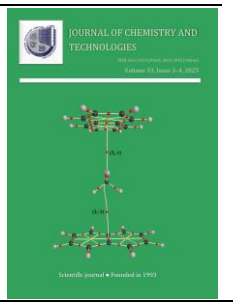

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STUDY OF KINETIC REGULARITIES OF HETEROCATALYTIC OXIDATION REACTIONS OF CHLOROHYDROCARBONS C_6, C_7

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Abstract

The kinetic regularities of the oxidation reaction of chlorotoluenes and chlorobenzenes on vanadium-containing catalysts have been studied, and on this basis, methods have been developed to control the activity and selectivity of ChCs (chlorohydrocarbons) oxidation processes. It has been shown that the oxidation rate of chlorohydrocarbons gradually increases with increasing temperature and contact time. It has been established that the oxidation processes of chlorohydrocarbons proceed through parallel-consecutive reactions with the formation of chlorine and dichloromaleic anhydrides and deep oxidation products. The presence, position and number of chlorine atoms affect the direction of the oxidation reaction. It has been shown that the rate of oxidation of chlorohydrocarbons to CO_2 on a fixed catalyst bed is higher than on a fluidized bed, although the rate of formation of the targeted products on a fluidized bed is higher. It has been established that both the initial chlorohydrocarbons and their oxidation products are compactly adsorbed on the surface of vanadium-phosphorous catalysts. The reaction products are stable to decomposition and have a significant effect on the oxidation kinetics of chlorohydrocarbons. It has been revealed that the main end products (CO_2, MCMA, DCMA), as well as some intermediate compounds, have a modifying effect on the active centers of the catalyst increasing the rate of selective oxidation of ChCs. It has been determined that the selective catalytic oxidation of CO occurs at ratios of CO : O_2 = 1 : 15 and higher, high catalysis rates are also observed at these ratios. It has been shown that during the oxidation of chlorobenzenes, MCMA and DCMA are formed, whereas during the oxidation of chlorotoluenes, chlorobenzaldehyde is also formed in addition to the above-listed compounds. The water formed in the oxidation reaction of chlorobenzenes and chlorotoluenes has a positive effect on active catalysts up to a certain concentration, modifying the active centers.

Keywords: kinetic regularity; chlorotoluene; chlorobenzene; oxidation reaction; catalyst.

ДОСЛІДЖЕННЯ КІНЕТИЧНИХ ЗАКОНОМІРНОСТЕЙ ГЕТЕРОКАТАЛІТИЧНИХ РЕАКЦІЙ ОКИСНЕННЯ ХЛОРОВУГЛЕВОДНІВ C_6, C_7

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Анотація

Вивчені кінетичні закономірності реакції окиснення хлоротолуолів і хлорбензолів на ванадійвмісних каталізаторах, і на цій основі розроблено методи керування активністю та селективністю процесів окиснення хлорвуглеводнів. Показано, що швидкість окиснення поступово зростає з підвищенням температури і часу контакту. Встановлено, що процеси окиснення протікають через паралельно-послідовні реакції з утворенням хлорного і дихлормалеїнового ангідридів та продуктів глибокого окиснення. Присутність, положення і кількість атомів хлору впливають на напрямок реакції окиснення. Показано, що швидкість окиснення до CO_2 на нерухомому шарі каталізатора вища, ніж на псевдозрідженому шарі, хоча швидкість утворення цільових продуктів на псевдозрідженому шарі вища. Встановлено, що на поверхні ванадій-фосфорних каталізаторів компактно адсорбуються як вихідні хлорвуглеводні, так і продукти їх окиснення. Продукти реакції стійкі до розкладу і суттєво впливають на кінетику окиснення хлоровуглеводнів. Основні кінцеві продукти (CO_2, MCMA, DCMA), а також деякі проміжні сполуки чинять модифікуючий вплив на активні центри каталізатора. Встановлено, що селективне каталітичне окиснення CO відбувається за співвідношень CO : O_2 = 1 : 15 і вище, коли також спостерігаються високі швидкості каталізу. Показано, що після окиснення хлорбензолів утворюються MCMA і DCMA, а окиснення інших хлоротолуолів призводить до утворення хлорбензальдегіду. Вода, що утворюється в реакції окиснення хлорбензолів і хлоротолуолів, до певної концентрації позитивно впливає на активні каталізатори, модифікуючи активні центри.

Ключові слова: кінетична закономірність; хлоротолуол; хлорбензол; реакція окиснення; каталізатор.

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Introduction

Over the last decade, heterogeneous catalytic oxidation of hydrocarbons and their chlorine derivatives has taken one of the central places in modern chemical and petrochemical science. This was facilitated by deep research conducted in this area, including the study of elementary acts and stages of catalysis [1–4].

The study of kinetic regularities and mechanism of catalytic reactions has allowed us to accumulate a wealth of experimental material for theoretical generalizations, which contributes to developing general concepts and theories of catalysis. Despite the high level of development of oxidative heterogeneous catalysis, a number of classes of compounds and derivatives of hydrocarbons that could be of interest for catalysis have not yet been objects of research. One such object is the widespread halogen-, in particular, chlorine-containing hydrocarbons obtained from raw materials of petroleum hydrocarbons [5–7].

It is known that polychlorinated aromatic hydrocarbons (PCAH) are toxic substances with high resistance to various aggressive environments, such as acidic, alkaline environments, and high temperatures [8; 9]. These compounds pollute the environment; they, when they enter the human body, they accumulate and cause various diseases. Although chlorobenzenes and chlorotoluenes obtained during decomposition of PCAH are less toxic than PCAH, they also pollute the environment.

High-temperature decomposition produces chlorine-containing aromatic compounds such as chlorobenzenes and chlorotoluenes; the release of vapors of these products into the environment is undesirable. It is not possible to process these substances using conventional methods. Therefore, a promising way to neutralize them is their catalytic oxidation to CO_2 and Cl_2 with their subsequent entrapping, as well as synthesis of valuable products of petrochemistry, such as chloro-derivatives of maleic anhydrous. However, the lack of active catalysts does not allow realization of these processes.

When conducting heterogeneous catalytic reactions, one of the main points is the choice of research methods that provide maximum information about the rate of the stages, the nature of the surface components and active centers on the catalyst surface, as well as accurate analyses. Based on the above, the aim of our research is the catalytic oxidation of chloroaromatic hydrocarbons not only to CO_2, but also to obtain chlorine and mono- and dichloromaleic anhydrides.

Experimental part

We synthesized catalysts based on V, P, Mo, Co oxides supported on Al_2O_3 and SiO_2, which allowed carrying out the oxidation process at temperatures of 673–773 K. At the same time, along with CO_2, we obtained valuable, abundantly used petrochemical products such as chlorinated maleic anhydride [10].

The main attention was paid to the synthesis of vanadium-phosphorus catalyst. The synthesis is carried out as follows: 100 g of 85 % orthophosphate acid (specific gravity 1.68) and 300 ml of H_2O are added into the reflux condenser flask stirring and heating constantly and then 40 g of oxalic acid are added. 30 g of V_2O_5 are gradually added to the hot solution in small portions. Each subsequent portion of V_2O_5 is added after the cessation of CO_2 releasing, which characterizes the reduction of V_2O_5. After the reduction of V_2O_5 is complete, 10 g of oxalic acid and 100 ml of H_2O are added and stirred until the cessation of CO_2 releasing. Further processing depends on the task in hand. If it is necessary to support the catalyst to some substrates, such as SiO_2, Al_2O_3, alundum, pumice stone, etc., then they are filled up with a hot solution of vanadium phosphate so that the entire substrate is covered with them. The spherical silica gel used as a substrate (industrial silica gel from the production of synthetic alcohol) was exposed to the hydrothermal treatment with high-pressure water vapor (up to 20 atm.) to increase the pore radius from 60–70 Å to 230 Å, which led to an increase in the specific surface area and facilitated the application of the active mass.

After applying the active mass, the catalyst is left for setting-out for 3 hours, filtered through a Schott filter, and then dried in a drying cabinet at a temperature of 433–453 K until moisture is removed. During moisture removal, the color of the catalyst changes from blue-green to dark gray. The catalytic system is calcined at first for 4–6 hours at a temperature of 523–573 K, then at 673–723 K for 3–4 hours. The catalyst is then crushed and sieved; the required fraction (0.5–0.6 mm or 0.25–0.5 mm or 0.6–0.8 mm) is loaded into the reactor. Activation is carried out in the same place for 4–6 hours with air at a temperature of 673–773 K, sometimes with the addition of chlorohydrocarbons to the flow.

It has been previously established that both the calcination temperature and calcination duration

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affect the activity and especially the selectivity of the synthesized catalysts. Optimal calcination conditions have been preliminarily selected for each catalytic system. Apparently, this affects the formation of the active phase of the catalysts [11].

X-ray phase analysis of the synthesized catalyst samples was carried out. According to X-ray diffraction, when the main components of the catalyst are taken in different V : P : Mo ratios, V_2O_5, P_2O_5, V_2MoO_8 phases are formed, and as the Mo content increases, MoO_3 and $V_9Mo_6O_8$ phases are also formed here. High activity and selectivity are due to the presence of the $V_9Mo_6O_8$ phase. According to the IR spectrum of the newly synthesized V-P-O/SiO_2 catalyst sample, absorption bands characteristic of Si-O-Si, P-O-P, V-O, V-OH and H-OH groups are observed. After the oxidation of o-dichlorobenzene on V-P-O/Al_2O_3, the intensity of the 1570–1580; 1470 and 1570 cm^{-1} spectra in the IR spectrum curve decreases, and the intensification of the absorption band at 1700 cm^{-1} specific to -C=O and the formation of the new band at 1120–1125 cm^{-1} specific to C-Cl prove the formation of the chlorinated maleate structure. Based on derivatographic studies, it was determined that there are physical, weak, medium and strong electron acceptor and oxidizing centers on the surface of the catalyst samples. After butylamine was adsorbed on the surface of the V-P-O/Al_2O_3+MoO_3 catalyst, endothermic effects were observed at 140, 180, 320, 500 °C on the DTA curve. Endothermic effects corresponding to temperatures of 60 (physical desorption), 160 (weak adsorption), 320 (medium proton-donor center) and 500 °C (strong electron-acceptor center) are observed on the DTG curve. Of the numerous catalysts analyzed, V-P-O (Mo) has the most active centers and shows high activity in the oxidation of the chlorinated compounds.

The study of the kinetics of chemical reactions in an enclosed volume, as well as the static method in instrumentation is described in detail in [12–14]. Also, the circulation method of studying kinetics, excluding external diffusion factors is described in detail [15] within the framework of the static method. Despite its great potential, the static method (integral nature) does not provide precise control over changes in catalyst activity.

Studying the kinetics of a reaction in a flow system allows it to be carried out in a stationary mode, which means that all quantitative characteristics of the system remain unchanged over time at each given point in the reaction space [16–18].

Experiments for the study of the influence of various variable parameters and kinetic features of heterogeneous catalytic oxidation of chlorohydrocarbons on various catalytic systems were carried out in laboratory setups using reactors with both fixed and fluidized catalyst beds.

Oxidation of chlorobenzenes and chlorotoluenes was carried out on the surface of V–P–O/Al_2O_3, V–Mo–O/Al_2O_3, V–Mo–O/SiO_2, V–P–O/SiO_2 catalytic systems. 1-monochlorobenzene (MCB), 1,2-dichlorobenzene (DCB), 1,3,5-trichlorobenzene (TCB), 2-monochlorotoluene (MCT), 2,3-, 2,4- and 2,5-dichlorotoluene (DCT) were subjected to oxidation [15; 18].

The composition of the main components in V–P–O and V–Mo–O catalysts is as follows: V_2O_5:P_2O_5 =1.1:1; V_2O_5:MoO_3=1.0:1.0; and 10 % of each oxide are applied to 80 % Al_2O_3 and SiO_2. The catalysts were also synthesized from the corresponding nitrate salts using the known method and applied on Al_2O_3 and SiO_2 by subsequent heat treatment [19].

The diagram of the flow laboratory setup for the oxidation of chlorohydrocarbons is shown in Fig. 1.

Air (or O_2 and N_2) for oxidation of CH (chlorohydrocarbons) at different CH : O_2 ratios, passing through the corresponding desiccants (3) and mixer (5), are heated (6) and fed into the reactor (9) with a fluidized (or fixed) catalyst bed. The oxidizing CH is fed there also through a syringe dispenser (8) and an evaporator (7). The temperature in the reactor is measured with a thermocouple placed in a "pocket". The reaction gases separated off from the reactor enter ice traps (10); here, the resulting oxidation reaction products and the unreacted portion of the CH are captured. The uncondensed portion of the reaction mixture enters successive traps (12, 13) for chemical analysis of the resulting Cl_2 and CO_2. After absorption of resulting Cl_2 by potassium iodide, CO_2 can also be analyzed chromatographically (15).

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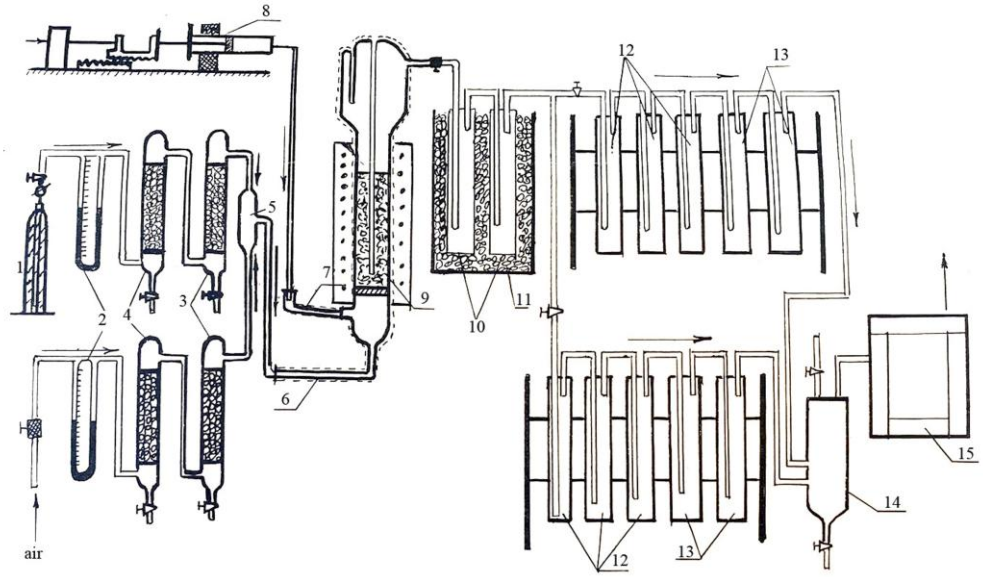

Fig. 1. Scheme of experimental laboratory setup for chlorotoluene oxidation. 1 – N_2 cylinder, 2 – rheometers, 3 – Al_2O_3 desiccants, 4 – $CaCl_2$ desiccants, 5 – mixer, 6 – air+N_2 heater, 7 – evaporator for chlorotoluene (chlorobenzene), 8 – automatic dosemeter (syringe dispenser), 9 – fluidized-bed reactor, 10 – traps for products, 11 – ice refrigerator, 12 – KJ traps for Cl_2, 13 – KOH traps for CO_2, 14 – CO_2 sampler, 15 – chromatograph for the analysis

The implementation of heterogeneous catalytic reactions carried out by flow and flow-circulation methods in a stationary mode, facilitates kinetic and mathematical descriptions of the process pattern [20; 21]. It is noted that the reaction occurs on the surface of a solid state, where the component concentration of the mixture differs in the core and the gas flow.

The study of the kinetics of the oxidation reaction of chlorohydrocarbons is important for establishing the direction and mechanism of their oxidation, as well as for modelling of kinetics for further optimization and design of the technological process [22; 23].

Results and their discussion

As already noted, the objects of the study were chlorotoluenes and chlorobenzenes. The study of the kinetic patterns of these compounds is of particular interest, since the role of the aromatic ring and the number and location of chlorine atoms in the molecules during the formation of monochloromaleic (MCMA) and dichloromaleic (DCMA) anhydrides are revealed. It is also important to determine the conditions for the reactions of selective and deep oxidation and to compare the deep oxidation rate with the selective formation reaction rate of the target products.

The influence of temperatures in the range of 673–773 K, contact time within 0.2–1.2 sec., concentration of chlorobenzenes and chlorotoluenes of $2.0\cdot10^{-3}$–$8.0\cdot10^{-4}$ mol/L, oxygen concentration of $1.0\cdot10^{-3}$–$8.0\cdot10^{-4}$ mol/L on the oxidation kinetics was studied. The kinetic curves of chlorotoluene oxidation are shown in Fig. 2.

As is seen from the figure, the oxidation rate of the initial chlorotoluene gradually increases with an increase in the contact time of 0.3–1.2 sec, and at the same time the rates of MCMA and CO_2 formation increase.

The rate of the deep oxidation reaction exceeds the rate of the main MCMA formation reaction by more than 3 times, however, on the graphs of these rates, some parallels is observed up to the contact time τ=0.6 sec., and then the rates increase sharply. The description of the results in coordinates for the corresponding substances shows that the dependence is linear (Fig. 2b). A comparison of the rates of deep and partial oxidation reactions shows that CO_2 is formed mainly from the initial chlorotoluene (CT). The selectivity to CO_2 decreases to τ = 0.8 sec., and then begins to increase due to the formation of CO_2 from the resulting target product (Fig. 2c), which proves that the oxidation reaction proceeds according to a parallel-sequential scheme.

The results of studying the kinetic regularities of the oxidation reaction of monochlorobenzene (MCB) are presented in Fig. 3. As is seen from the presented dependencies, the oxidation rate of the initial MCB is more than 3 times higher than the formation rate of DCMA and is comparable with the formation rate of CO_2 (a). Carbon dioxide is formed at the beginning of the oxidation reaction of initial MCB and further, as well as at small values of the contact time τ, but a sharp discontinuity in the rate of CO_2 formation is observed after τ=0.7 sec.

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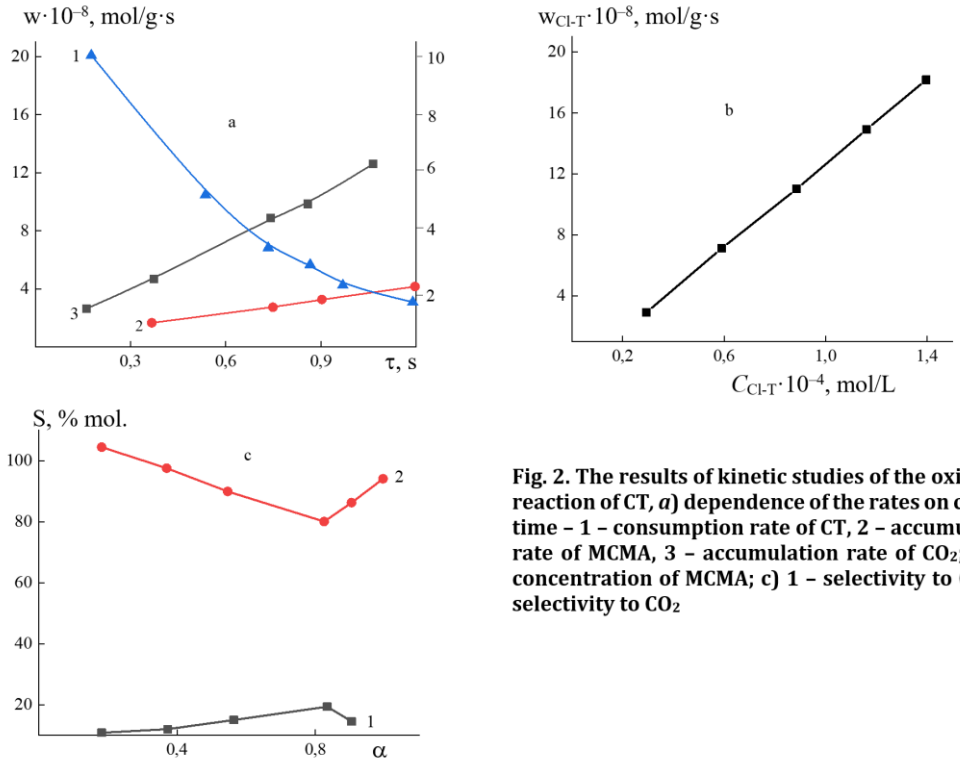

Fig. 2. The results of kinetic studies of the oxidation reaction of CT, *a*) dependence of the rates on contact time – 1 – consumption rate of CT, 2 – accumulation rate of MCMA, 3 – accumulation rate of CO_2; b) on concentration of MCMA; c) 1 – selectivity to CT, 2 – selectivity to CO_2

α – conversion of chlorobenzenes and chlorotoluenes.

The rate curve of the chlorine formation behaves similarly to the rate curve of CO_2 formation, which confirms the view that an additional path of CO_2 is formed from the resulting chlorine-containing compound. The dependences of the CO_2 and Cl_2 formation rates on their concentrations rise in parallel at close values. A comparison of the formation reaction rate of the main DCMA and the deep oxidation reaction rate shows that CO_2 is formed according to a parallel-consecutive scheme both from the initial compounds and from the target product under certain conditions, which follows from the analysis of the dependence of selectivity on conversion. (3b kommentariy).

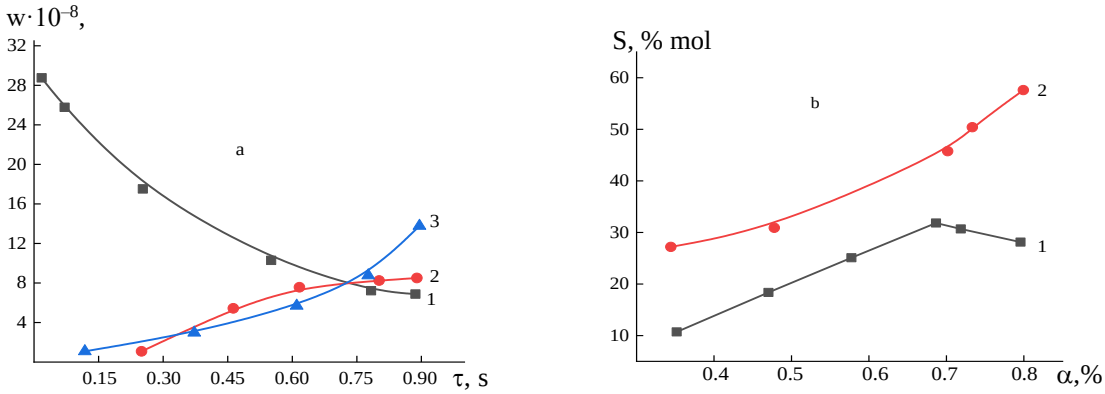

Fig. 3. The results of kinetic studies of oxidation reaction of MCB, (*a*) dependence of the rates on contact time 1-MCB, 2-MCMA, 3-Cl_2; (b) dependence of selectivity on conversion of MCB, 1-MCMA, 2-CO_2
Kat.: V–P–O/SiO_2; T=733K, xt÷0=1÷20

The study of the kinetics of dichlorobenzenes and trichlorobenzenes confirms the above assumption about the formation of MCMA and CO_2. The dependencies established for CT and MCB were preserved in this case as well. A comparison of the rates of the main reaction and the deep oxidation reaction here indicates the parallel-consecutive pathway of CO_2 formation.

The V–P–O/Al_2O_3+MoO_3 system has been studied for a wide range of V:P:O ratios.

The results given in Table 1 show that, in the oxidation reaction of 1,2-DCB, V–Mo–O/SiO_2, V–Mo–O/Al_2O_3 and V–P–O/Al_2O_3 catalytic systems

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exhibit high activity and selectivity. Therefore, we have studied the activity and selectivity of these catalytic systems promoted with MoO_3 and P_2O_5 in the oxidation reaction of 1,2-DCB according to our previous studies. In the ranges of temperature 653-753K, contact time τ=0.3–1.1 sec, and ratio of 1,2-DCB : O_2=1:5–1:20 mol, the effect of these parameters on the oxidation of 1,2-DCB was studied with V–P–O/SiO_2+MoO_3, V–P–O/Al_2O_3 +MoO_3 and V–Mo–O/Al_2O_3+P_2O_5 catalytic systems.

Table 1

Effect of the ratio of active components of the catalyst on the oxidation reaction of 1,2-DCB

Catalytic systems	Ratio of the oxides V_2O_5:P_2O_5,MoO_3:V_2O_5	Conversion of 1,2-DCB	Selectivity, mol%		
			DCMA	MCMA	MA
V–P–O/SiO_2	1:1	80	30	14	5
V–P–O/SiO_2	1:2	84	38	20	6
V–P–O/SiO_2	1:3	88	36	15	5
V–Mo–O/SiO_2	1:1	82	32	16	6
V–Mo–O/SiO_2	1:2	92	42	18	6
V–Mo–O/SiO_2	1:3	94	46	20	7
V–P–O/Al_2O_3	1:1	85	36	13	6
V–P–O/Al_2O_3	1:2	90	40	12	5
V–P–O/Al_2O_3	1:3	92	36	14	4
V–Mo–O/Al_2O_3	1:1	87	35	10	5
V–Mo–O/Al_2O_3	1:2	94	45	18	8
V–Mo–O/Al_2O_3	1:3	98	50	24	10

The graphical presentation of the effect of two parameters on the conversion is shown in Fig. 4. The results show that the conversion of 1,2-DCB reaches 100 % with an increase in temperature from 653–753 K in the presence of the V–Mo–O/Al_2O_3+P_2O_5 catalytic system at T=713 K (Fig. 4a), while the maximum conversion of 1,2-DCB can be achieved at a contact time of 0.7–0.8 sec. (Fig. 4 b). A study of the dependence of the selectivity of these catalytic systems on the contact time and the DCB : O_2 mole ratio also showed that a 50 % selectivity of DCMA, which is considered the main product of the oxidation of 1,2-DCB, was achieved in the presence of the V-Mo-O/Al_2O_3+P_2O_5 catalyst at a temperature of 713 K, a contact time of 0.7 sec. and a 1,2-DCB : O_2 ratio of 1 : 15.

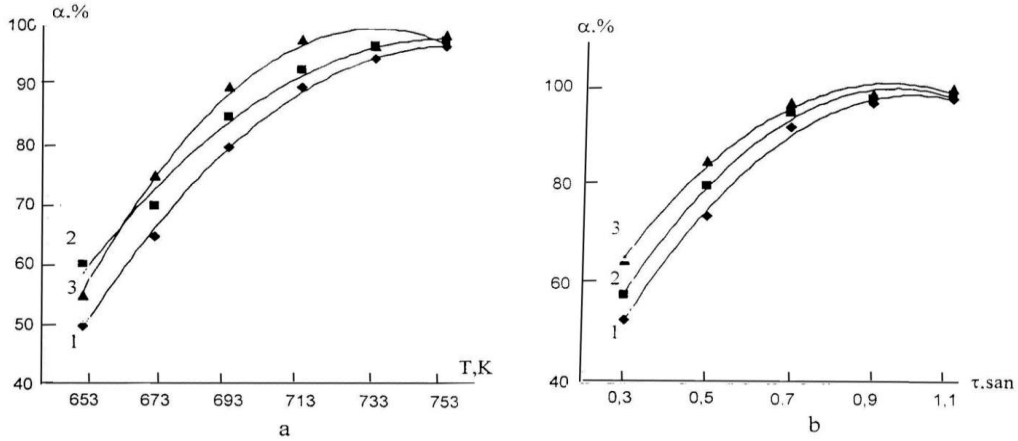

Fig. 4. Effect of temperature (a) and contact time (b,) on activity (a, b) of catalytic systems in the oxidation reaction of 1,2-DCB. 1–V–P–O/SiO_2+MoO_3, 2–V–P–O/Al_2O_3+MoO_3, 3–V–Mo–O/Al_2O_3+P_2O_5

Then, we studied the effect of the contact time variation in the range of 0.2–1.2 sec. on the oxidation reaction of 1,2-DCB. The obtained results (Fig. 5) show that the conversion of 1,2-DCB is relatively low (40–68 %) and 1,2-DCB is mainly oxidized to CO_2 at low contact times (0.2–0.4 sec.). At contact times of 0.6–0.8 sec., the conversion of DCB reaches 90–100 %, and at this time the selectivity of DCMA and also MCMA increases to 46–48 %, and selectivity reaches 50 % at τ=0.7 sec. A further increase in contact time is observed with a decrease in the selectivity of hydrochloric anhydrides at a conversion value of 100 %, which can be explained by the oxidation of hydrochloric anhydrides to CO_2. Thus, the yield of CO_2 begins to increase rapidly at these contact times.

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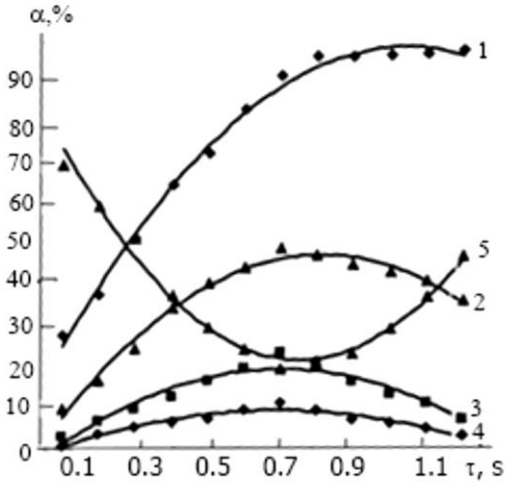

Fig. 5. Effect of contact time on the oxidation reaction of 1,2-DCB: 1 – conversion of 1,2-DCB, 2 – selectivity to DCMA, 3 – selectivity to MCMA, 4 – selectivity to MA, 5– selectivity to CO_2, V=4000 hour^{-1}, τ=0.7 sec., DCB : O_2=1 : 20

The oxidation reaction of trichlorobenzenes (TCB) was carried out in a fluidized bed of an open flow reactor on the catalytic systems that we synthesized V–P–O/SiO_2, V–P–O/Al_2O_3, V–Mo–O/SiO_2, V–Mo–O/Al_2O_3, V–P–O/SiO_2+MoO_3, V–Mo–O/Al_2O_3+P_2O_5, V–P–O/SiO_2+Co_2O_3.

We have determined the activities of these catalytic systems in the oxidation reaction of 1,2,4-TCB (or 1,2,3-TCB and 1,3,5-TCB) at different ranges of some parameters, temperature of 673–773 K, contact time of 0.2–1.0 sec, and TCB : O_2 = 1 : 1÷1 : 30 mol ratios.

The results are given in Figure 6. As is seen from the results, the conversion during oxidation of chlorinated hydrocarbons reaches its maximum degree mainly at high temperatures of 753, 773 K and 0.8–0.9 sec. contact time with the catalyst based on V–Mo–O/Al_2O_3 (2, 4, 5). When Mo is added to these systems (3, 4), the catalytic systems reach their maximum activity values at relatively low temperatures (733 K) and contact time (0.7 sec.). The cobalt promoted-catalyst (6) does not show very high activity compared to other systems.

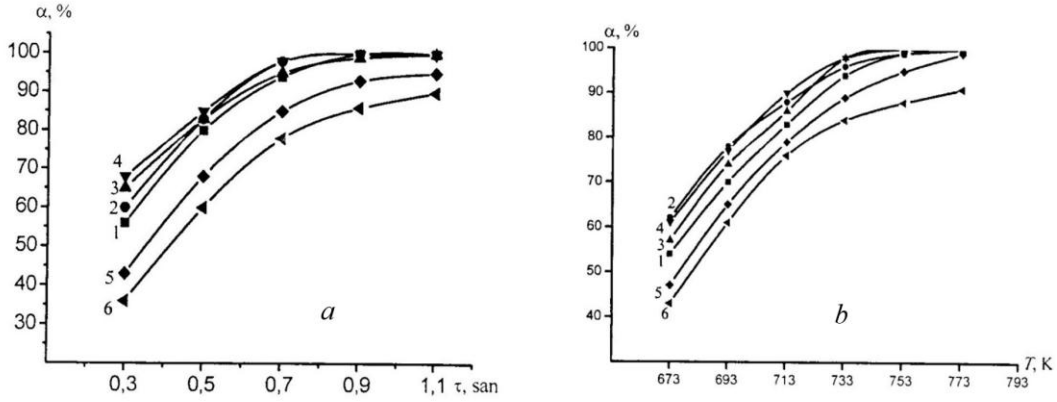

Fig. 6. Effect of temperature (a) and contact time (b) on the activities of the catalytic systems in the oxidation reaction of 1,3,5-TCB: 1–V–P–O/SiO_2, 2–V–Mo–O/Al_2O_3, 3–V–P–O/SiO_2+MoO_3, 4–V–Mo–O/Al_2O_3+MoO_3, 5–V–Mo–O/Al_2O_3+P_2O_5, 6–V–P–O/SiO_2+Co_2O_3.

At the same time, the maximum values of chloranhydrides are achieved at a contact time of 0.7 sec. in the oxidation of 1,3,5-TCB (for 1,2,4-TCB, at 0.7 sec.). The selectivity of chloranhydrides also reaches a maximum at a molar ratio of chlorobenzene to oxygen of 1:20. The selectivity of the anhydrides decreases at 753–773 K and at the values of contact times higher than 0.7–0.8 sec., which is explained by their own oxidation.

Thus, as a result of the studies, the activity order of the catalytic systems used in the oxidation reaction of 1,3,5-TCB were mainly determined as follows: V–Mo–O/Al_2O_3+MoO_3>V–P–O/SiO_2+MoO_3>V–P–O/SiO_2>V–Mo–O/Al_2O_3+ +P_2O_5>V–P–O/SiO_2+Co_2O_3; and selectivity order V–P–O/Al_2O_3+MoO_3>V–Mo–O/Al_2O_3+P_2O_5>V–P–O/SiO_2+MoO_3>V–Mo–O/Al_2O_3>V–P–O/SiO_2>V–P–O/SiO_2+Co_2O_3; in the oxidation reaction of 1,2,4-TCB – activity order V–Mo–O/Al_2O_3+MoO_3>V–P–O/SiO_2+MoO_3>V–P–O/SiO_2>V–Mo–O/Al_2O_3+ P_2O_5>V–P–O/SiO_2+Co_2O_3; selectivity order V–P–O/Al_2O_3+MoO_3>V–P–O/SiO_2+MoO_3>V–Mo–O/ Al_2O_3>V–Mo–O/Al_2O_3+P_2O_5>V–P–O/SiO_2>V–P–O/SiO_2+Co_2O_3.

It should be noted that the activity order of the catalytic systems was implemented for the distribution of reaction products obtained in the process of oxidation of dichlorotoluenes. High conversion and low yield of the reaction products were observed only on unmodified catalytic systems in 2,4-DCT oxidation, as in the case of monochlorotoluenes.

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According to the results, it was determined that the yields of DCMA, MA and CBA (chlorinated benzoic acid) were 38 %, 14 % and 10–12 %, respectively, in 3,4-DCT oxidation in the presence of the molybdenum-modified catalytic system V–P–O/SiO_2+Mo (Table 2). At this case, the conversion of 3,4-DCT was 90 %. The yields of selective oxidation products slightly decreased with increasing conversion, due to which the yield of CO_2 increased.

Similarly, the selective oxidation of 2,3-, 2,4-, and 2,5-DCT was carried out in the presence of V–Mo–O/SiO_2+V, V–P–O/Al_2O_3+Mo, V–P–O/Al_2O_3+Sb catalytic systems. The obtained results are given in Figure 7 and Table 2.

Table 2

General process pattern of 2,4-dichlorotoluene oxidation

Selected components and oxides	Supports	Reaction temperature, T, K	Contact time, sec.	2,4-DCT:O_2 mol ratio	Conversion of 2,4-DCT %	Oxidation products			
						CBA	MA	MCMA	CO_2
V_2O_5 MoO_3 P_2O_5 Sb_2O_3	–	713	0.7	1:15	60	–	16	12	28
	–	723	0.6	1:10	55	–	13	10	30
	–	703	0.6	1:15	45	–	10	5	28
	–	693	0.6	1:10	38	–	5	5	20
V_2O_5 MoO_3 P_2O_5 Sb_2O_3	SiO_2	713	0.7	1:20	64	5	16	14	28
	SiO_2	723	0.8	1:20	60	–	13	12	26
	SiO_2	693	0.6	1:10	45	–	10	8	24
	SiO_2	693	0.6	1:10	40	–	6	–	30
V_2O_5 MoO_3 P_2O_5 Sb_2O_3	Al_2O_3	723	0.7	1:20	68	4	18	13	30
	Al_2O_3	733	0.8	1:20	64	–	14	12	28
	Al_2O_3	693	0.6	1:10	48	–	10	7	27
	Al_2O_3	693	0.6	1:10	44	–	5	–	32
V_2O_5- P_2O_5 V_2O_5- P_2O_5 V_2O_5-MoO_3 V_2O_5-MoO_3 V_2O_5-Sb_2O_3 V_2O_5-Sb_2O_3 $VMoO_3$·Sb_2O_3 MoO_3·Sb_2O_3	SiO_2	713	0.7	1:15	76	8	15	26	28
	Al_2O_3	723	0.7	1:20	78	4	12	20	33
	SiO_2	723	0.8	1:15	74	4	11	24	32
	Al_2O_3	713	0.8	1:20	76	3	10	20	36
	SiO_2	693	0.6	1:15	68	5	10	22	26
	Al_2O_3	703	0.6	1:10	70	3	8	16	28
	SiO_2	693	0.6	1:18	66	–	6	15	34
	Al_2O_3	703	0.7	1:10	65	–	5	12	36

The temperature, contact time and mole ratio (DCT : O_2) dependences of the oxidation products of 2,4- and 2,5-DCT were studied over a wide range of these parameters in the presence of the V–P–O/SiO_2+Mo catalyst. The obtained results are reflected in Table 2.

Analysis of the results shows that in the temperature range of 653–733 K, the conversion of dichlorotoluenes increased from 38 % to 78 %. At this time, the yields of MCMA, MA, CBA and CO_2 increased to 24–26 %, 18–20 %, 8–10 % and 36 %, respectively.

The contact time variation in the 0.2–1.0 sec. range did not change the overall picture much. Thus, the conversion of dichlorotoluenes increased from 40 % to 80 %, while the yields of other oxygenated products showed a relative increase in accordance with a general pattern and decreased at a contact time of 0.6–0.7 sec. after passing through a maximum.

The results show that the oxidation products are mainly DCMA where the number and position of chlorine atoms in chlorobenzene and chlorotoluene molecules is 1, 2-; 3, 4- and 1,2,4-; and MCMA is obtained in the cases where the number and position of chlorine atoms in chlorobenzene and chlorotoluene molecules is 1-; 1,3-; 2,4-; 2,5- and 1,3,5-. At the same time, as the number of chlorine atoms in the aromatic molecule increases, the conversion of the initial chlorinated compounds decreases, but the selectivity of the targeted product increases.

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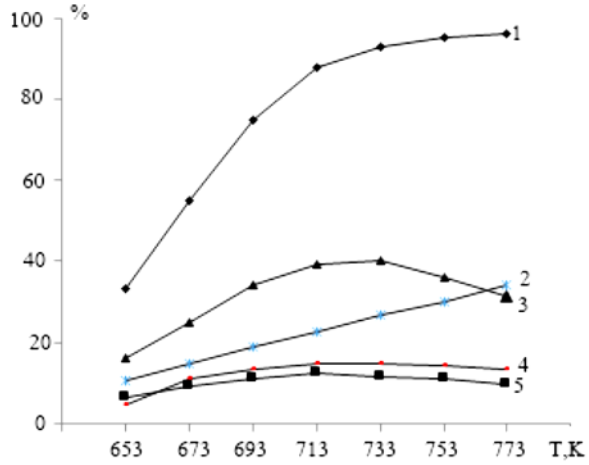

Fig. 7. Temperature effect of the catalytic oxidation reaction of dichlorotoluenes: oxidation of 2,3-DCT in the presence of V–Mo–O/SiO_2+V. 1 – DCT, 2 – MCMA, 3 – MA, 4 – CBA, 5 – CO_2

As is seen from the results, the highest selectivity among these catalytic systems is shown by the V–P–O/SiO_2+Mo catalyst. At this point, with a contact time of 0.7 seconds, the yield exceeds the maximum and increases to 40–42 %.

The activity order of the catalysts in 2,4-DCT oxidation is as follows:

V–P–O/SiO_2+Mo>V–P–O/$A1_2O_3$+Mo>V–Mo–O/Al_2O_3+Mo,

The selectivity order:

V–P–O/SiO_2+Sb>V–P–O/$A1_2O_3$+Mo>V–Mo–O/Al_2O_3+P>V–P–O/SiO_2+Mo.

These studies were also carried out varying the DCT : O_2 mole ratio from 1 : 5 to 1 : 25. In this case, the maximum result was achieved at DCT : O_2=1 : 15 mole ratio, and it was determined that the yields of the main products is: MCMA 33–35 %, MA 13–15 %, and CBA 8–10 %.

Thus, the study of kinetic regularities of the oxidation reaction of chlorine-containing aromatic and hydrocarbons on the surface of vanadium-phosphorus catalysts showed that they are of a same nature. The comparison of the formation rates of the deep oxidation products and target compounds clearly indicates the presence of two formation pathways – parallel-consecutive. The rate of formation of free chlorine and the rate of formation of CO_2 are commensurable, especially at certain values of contact time and temperature, which once again confirms the idea of the presence of an additional path for the formation of CO_2 from both the target products and the initial chlorine-containing compounds. The comparison of the rates of formation of the target products confirms the correct choice of a fluidized bed of catalyst for the reactions under study. It was found that the final reaction products do not have an inhibitory effect on the rate of oxidation reactions.

All necessary calculations were performed using the software package “Optim Me” [24; 25].

Conclusion

1. Active catalysts and basic technological schemes for heterogeneous catalytic oxidation of chlorinated hydrocarbons have been developed, yielding valuable polyfunctional compounds such as mono- and dichloromaleic anhydride, and waste from the production of polychlorinated hydrocarbons has been utilized.

2. The kinetic regularities of the oxidation reaction of various chlorobenzenes and chlorotoluenes on V–P–O/SiO_2, V–Mo–O/Al_2O_3 catalysts have been studied, and it has been established that the oxidation process occurs according to a parallel-sequential scheme. Active catalytic systems based on V and Mo oxides has been obtained for the heterogeneous catalytic oxidation reaction of chloroaromatic hydrocarbons, and a basic process flow chart has been developed. In this case, valuable polyfunctional compounds such as mono- and dichloromaleic anhydrides have been obtained, and waste has been utilized. Optimal process conditions have been established to ensure the maximum yield of targeted products.

3. It has been established that the heterogeneous catalytic oxidation processes of chlorohydrocarbons carried out in a fluidized bed of vanadium-molybdenum oxide catalysts are preferable for obtaining the targeted products. It has been shown that the position of chlorine atoms in the aromatic ring and their number affect the degree of conversion and selectivity of the process.

References

[1] Kiperman, S.A. (1964). *Introduction to the kinetics of heterogeneous catalytic reactions*. M.: Nauka, 514.

[2] Li, X., Chen, Y., Chen, Z, Guo, H, Yang, S., Ma, X. (2022). The recent progress on gaseous chlorinated aromatics removal for environmental applications. *Sep. Purif. Technol.* 121364. https://doi.org/10.1016/j.seppur.2022.121364

[3] Yang, L., Liu, P., Zhang, H.-Yu, Zhang, Y., Zhao, J. (2020). Catalytic Oxidation of *o*-Chlorotoluene with Oxygen to *o*-Chlorobenzaldehyde in a Microchannel Reactor. *J. Ame. Chem. Soc. 24*(10), 2034–2042, https://doi.org/10.1021/acs.oprd.0c00135

[4] Jacques, V. (2016). Heterogeneous catalytic partial oxidation of lower alkanes (C_1–C_6) on mixed metal oxides. *J. Energy Chem. Elsevier, 25*(6), 936–946. DOI: 10.1016/j.jechem.2016.10.007

[5] Melikova, I.G., Efendi, A.J., Aykan,N. F., Babayev E.M., Faradjev, G. M. and Rustamova, J. T. (2023). Catalysts and Kinetic Regularities of Oxidation Processes of Chlorotoluenes. *Eurasian Journal of Chemistry* , 4 (112), 134-140. https://doi.org/10.31489/2959-0663/4-23-3.

[6] Dong, Y., Gao, S., Feng, J., Wang, X., Zhu, K., Wu, K., Guo, R. (2024). Recent advances in catalytic oxidation of chlorobenzene over metal oxide-based catalysts. *Sep. Purif. Technol.,* 128098. https://doi.org/10.1016/j.seppur.2024.128098

[7] Torsten Klement, Schirin Hanf, Fabian Wolff , Norbert Kockmann, Stephan A. Schunk and Thorsten Röder (2021). Oscillating droplet reactor – towards kinetic investigations in heterogeneous catalysis on a droplet scale. *React. Chem. Eng.*, 6, 1023-1030. DOI: 10.1039/D0RE00466A

[8] Melikova, I. H. (2016). Oxidation of chlorotoluene, toluene and chlorobenzene in the presence of Ag/MnO_2 catalyst. *Azerbaijan Oil Industry, 202*(210), 47–52. doi: 10.37474/0365-8554/ 2022-10-47-52

[9] Liu, J., Liu, L., Zhang, W., Li, P., Li, X., Yu, Z., Su, W. (2023). Continuous catalytic aerobic oxidation of *o*-chlorotoluene to *o*-chlorobenzoic acid under slug flow conditions. *J. Flow Chemistry, 13*, 325–335. doi: 10.1007/s41981-023-00272-2

[10] Melikova, I.H., Efendiyev, A.J., Yunisova, F.A. (2001). Reactivity of chlorohydrocarbons in catalytic oxidation reactions. *Azerb. Chem. J., 2*, 13–18.

[11] Zhang, X., Hong, J., Zhang, Ch., Liu, Q., Zhang, J., Qian, G. (2022). Controlling effect of TiO2 carrier on formed vanadium species for effective catalytic oxidization of chlorobenzene. *J. Applied Surface Science*, *605*, 154643. https://doi.org/10.1016/j.apsusc.2022.154643
Zhang, T. (2020). *Heterogeneous Catalytic Process for Wastewater Treatment*. Advanced Oxidation Processes. DOI: 10.5772/intechopen.90393

[12] Dhakshinamoorthy, A., Alvaro, M., Garcia, H. (2011). Metal-organic frameworks as heterogeneous catalysts for oxidation reactions. *Catal. Sci. Technol., 1*(6), 856–867. https://doi.org/10.1039/C1CY00068C

[13] Xie, R., Cao, J., Xie, X., Lei, D., Guo, K., Liu, H., Zeng, Y., Huang, H. (2020). Mechanistic insights into complete oxidation of chlorobenzene to CO_2 via wet scrubber coupled with UV/PDS. *Chem. Eng. J., 401*, 126077. https://doi.org/10.1016/j.cej.2020.126077

[14] Babayev, E., Efendi, A., Aykan, N. (2014). Oxidation reactions of chlorobenzene and chlorotoluene in the presence of oxide catalysts. *World Forum of Young Scientists Collection of abstracts*, 143–145.

[15] Jacques, C.V. Heterogeneous Catalysis on Metal Oxides (2017). *Catalysts*, *7*(11), 341. https://doi.org/10.3390/catal7110341

[16] Melikova, I. G., Efendi, A. J., Aykan, N. F., Babayev, E. M., Farajev, G. M., Rustamova, C. T. (2023). Catalysts and kinetic regularities of oxidation processes of chlorotoluenes. *Eurasian Journal of Chemistry. 112*(4), 130–140; DOI:10.31489/2959-0663/4-23-3

[17] Qin, Y., Gu, J., Cai, W., Wang, Zh. (2022) Catalytic oxidation of chlorobenzene and PCDD/Fs over V_2O_5-WO_3/TiO_2: insights into the component effect and reaction mechanism. *J. Environ Sci. Pollut. Res. Int., 29*(28), 42809–42821. doi: 10.1007/s11356-022-18768-0.

[18] Salehli, N.F., Efendi, A.J., Melikova, I.H. et al. (2004). Catalytic oxidation reactions of 1,3,5- and 1,2,4-trichlorobenzenes. Azerb. Chem. J. 4, 88-94

[19] Li, W., Hu, D., Yin, K., Yu, Ch., Huang, B. (2022). Hierarchical Ru-Ce/H-ZSM-5 catalysts for the catalytic oxidation of chlorobenzene: Structure-activity relationship and chlorine poisoning resistance. *J. Surfaces and Interfaces, 34*, 102320

[20] Zhou, W., Chen, L., Xie, J. (2015). Efficient synthesis of p-chlorobenzaldehyde through liquid-phase oxidation of *p*-chlorotoluene using manganese-containing ZSM-5 as catalyst, *RSC Adv., 91*, 74162–74169. https://doi.org/10.1039/C5RA16206H

[21] Liu, J., Zhang, Y., Yan, X. Wang, Z., Wu, F., Fang, S., Jian, P. (2018). Selective oxidation of o-chlorotoluene to o-chlorobenzaldehyde catalyzed by $(Co,Mn)(Co,Mn)_2O_4$ catalysts. *The Canadian Journal of Chemical Engineering.,96*, 1746–1751. doi:10.1002/cjce.23116

[22] Melikova, I.H., Aykan, N.F., Efendi, A.J., Babayev, E.M., Faradjev, H.M., Yunisova, F.A., Nebiyeva, M.F. (2022). Kinetic regularities of the reaction of catalytic oxidation of aromatic chlorohydrocarbons. *Readings of A.I. Bulatov. Collection of Articles*, 103–106.

[23] Manafov, M.R. (2016). Software application for solving some typical problems of chemical technology. *Azerb. Chem. J., 2*, 89–94.

[24] Manafov, M. R. (2015). Development of a Software Application for Solving of Problems of Chemical Kinetics and its Implementation in a C#. *Int. J. Eng. Appl. Sci. 2*(10), 33–37.