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Article

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Catalysts and Kinetic Regularities of Oxidation Processes of Chlorotoluenes

The article is devoted to the selection, synthesis and study of the activities of the vanadium oxide-based catalytic systems supported on SiO_2 and Al_2O_3 carriers in the oxidation process of chlorotoluenes. It was shown that V-P-O/SiO_2+Mo, V-Mo-O/SiO_2+V, V-P-O/Al_2O_3+Sb, V-Mo-O/Al_2O_3+Mo catalytic systems exhibit high activity and selectivity in the processes of selective oxidation of mono- and dichlorotoluenes in the gas phase. The oxidation processes of chlorotoluenes were studied in open-type reactors with stationary and fluidized catalyst beds. It was established that the conversion of chlorotoluenes in a reactor with a stationary bed is higher than in a fluidized bed reactor, but selectivity in stationary bed it is slightly lower. The optimal conditions ensuring high conversion (80–95 %) and selectivity of the obtained chloromaleic anhydrides (40–45 %) were determined in a wide range of changes of technological parameters T=673–773 K, τ=0.1–1.0 s, molar ratios XT:O_2=1:1–1:25. It is established that the activities of the catalytic systems were different depending on the method of preparation. Thus, it was noticed that among the catalysts obtained by the methods of precipitation, mechano-chemical impregnation and co-precipitation-impregnation, the latter has shown satisfactory results.

Keywords: aromatic hydrocarbons, chlorotoluene, dichlorotoluenes, catalyst, kinetic regularities, catalytic systems, activity, selectivity.

Introduction

These days, when there is a rapid development in the petrochemical industry, it is very important to investigate the wide application areas of hydrocarbons and their chlorinated analogs. Among the heterogeneous catalytic oxidation processes of aromatic hydrocarbons in the gas phase, the most widespread reactions of benzene and toluene to maleic anhydrides [1–5] should be mentioned. For a long time, the conversion processes of a number of compounds with aromatic ring on various oxide catalysts have been already thoroughly studied and applied on an industrial scale. In accordance with this, the study of oxidation reactions of halogen-containing, especially chlorine-containing chlorotoluenes is of both theoretical and practical importance. The theoretical determination of the influence of chlorine atoms of chlorine-containing toluene and benzenes on the oxidation reactions, the interaction of chlorine with the surface of the catalyst, the effect of the chlorine–oxygen medium on the catalysis process, and developing the general catalysis theory of the processes, the kinetic regularities and mechanism of the oxidation reactions of chlorinated toluenes are of great interest.

A number of scientists [6–9] carried out the oxidation processes of chlororganic industrial waste to CO, CO_2, HCl in a fluidized bed reactor in the presence of catalysts of Mo, Co, Cr, Ni metals added as promoters to the Pd/Al_2O_3 system. Some scientists achieved the oxidation process of 2,4-dichlorobenzoic acid, which is widely used as an intermediate in the pharmaceutical industry of 2,4-dichlorotoluene in the presence of cobalt stearate catalyst. At the same time, a special chromatographic method was developed to study the process in detail. By this method, it is possible to analyze the reaction product after the process without performing any analytical cleaning procedure [10].

Oxygenated derivatives of toluene are used as valuable intermediate products in the manufacture of polymers, rubber, resins and dyes [11, 12]. Conversion of toluene and its derivatives to corresponding aldehydes is one of the most useful processes. These traditional conversion reactions with low conversion and selectivity carried out in the presence of dissolved heavy metal salts of acetic acid via a homogeneous process were shown in [13, 14].

In addition, such processes are economically inconvenient, and heavy metal-containing reaction products released during the process are considered to be dangerous for the environment due to the difficulty of separation of soluble catalysts [15–18].

The main goal of this work is the synthesis and selection of active and selective catalytic systems for the oxidation of chlorotoluenes to chlorine and chloromaleic anhydrides, as well as the neutralization of waste substances released into the environment.

Some of these catalysts consist of only individual oxides, for example, V_2O_5, MoO_3, Sb_2O_5, P_2O_5, CuO and the others compose of mechanical mixtures. The most common method of synthesis is application of soluble salts of these metals, which are easily decomposed during heating, namely, nitrates, ammonium compounds, chlorine-containing and acetate compounds. Therefore, synthesis of such catalytic systems were carried out based on the known methods using ammonium and nitrate salts of V, Mo, P, Sb [15, 16].

In general, the transformation of chlorobenzene and chlorotoluene into widely used compounds by catalytic oxidation should also be considered as a solution of the environmental problem.

Experimental

Initially, a number of catalytic systems were synthesized in order to apply them to the catalytic oxidation reactions of chlorotoluenes. These catalytic systems mainly consist of vanadium, phosphorus, molybdenum, stibium oxides deposited on Al_2O_3 and SiO_2 carriers. In some samples, these oxides are also added as promoters. Catalyst samples in our research were synthesized according to the following technique: The catalytic systems are mainly obtained from ammonium vanadate (NH_4VO_3), ammonium molybdate ($(NH_4)_6Mo_7O_2 \cdot 4H_2O$), sodium phosphate ($Na_2HPO_4 \cdot H_2O$) and orthophosphate salts, occasionally from vanadium nitrate, stibium nitrates, stibium chloride or $Sb_2O_5$by their dissolving in oxalic or HCl acid solutions. Depending on the synthesis method, the obtained solution can be deposited on Al_2O_3 or SiO_2 after its slight evaporation. After that, the obtained catalyst is heated in an air at a temperature of 453–533 K for 1 hour, then at 553–653 K for the next 2 hours, and then up to 773 K for 1 hour.

Thus, the synthesized catalyst samples were brought to working condition and their oxidation reactions were studied in both stationary and fluidized bed of open flow reactors.

Chlorotoluenes with a purity of ≥ 99.0 % and manufactured by Sigma Aldrich Company were used for the study of the heterogeneous catalytic oxidation process of chlorotoluenes in the gas phase.

The synthesized catalyst samples were studied by physicochemical analysis methods.

Prepared catalysts were characterized by X-ray phase diffraction, FT-IR, N_2 adsorption-desorption method, thermal analysis, elemental analysis and scanning electron microscope.

Phase formation processes, quantitative phase analysis, the properties of the phases were investigated based on the crystal structure of the synthesized catalytic systems and determined by X-ray D2 phase-X-ray diffraction analysis equipment manufactured by Bruker (Germany).

Information about the surface area (S_{bet}, m^2/g) and the pore area (total volume VΣ, cm^3/g, diameter d, Å) of the catalytic system were obtained from the adsorption-desorption isotherms at the liquid nitrogen (–196 °C) temperature (Gas adsorption analyzer for surface area and pore size). During the measurements, the samples were first degassed to 0.1Pa. From Brunauer Emmett Teller (B.E.T.) theory, surface area was calculated by its resemblance to the profile cross-section of 0.164 nm^2 corresponding to nitrogen.

Thermogravimetric analysis were carried out on a NETZSCH STA 449F3 (Germany) device programmed to 10 °C/min graduation in the temperature range of 25–900 °C. In this case, the weight of the investigated nanopowder sample was 0.6 g.

Results and Discussion

The results of the X-ray phase analysis of some studied systems are shown in Figure 1.

Figure 1a shows the result of the X-ray phase analysis of the V–P–O system with the ratio of the main componentsV:P=1:2 in the catalyst sample.

Figure 1b presents the X-ray phase diagram of the same catalyst sample on the Al_2O_3 substrate.

As is seen from figures, the $VO(PO_4)_2$ and $VOPO_4$ phases are mainly observed on the phase diagram. However, it was also determined that the phase formation process of $V–P–O/Al_2O_3$ catalyst arises from vanadium pentoxide (28.3 %), aluminum phosphate (19.2 %), AlPO (3 %), aluminum oxide (11.1 %), aluminum hexacyclophosphate (19.2 %) phases. The amorphous phase is the main part of the catalyst, mostly due to the use of Al_2O_3 as a carrier. At the same time, phases such as vanadium oxide and divanadium pentoxide dominate in the composition of the samples, which are responsible for the activity of the catalyst.

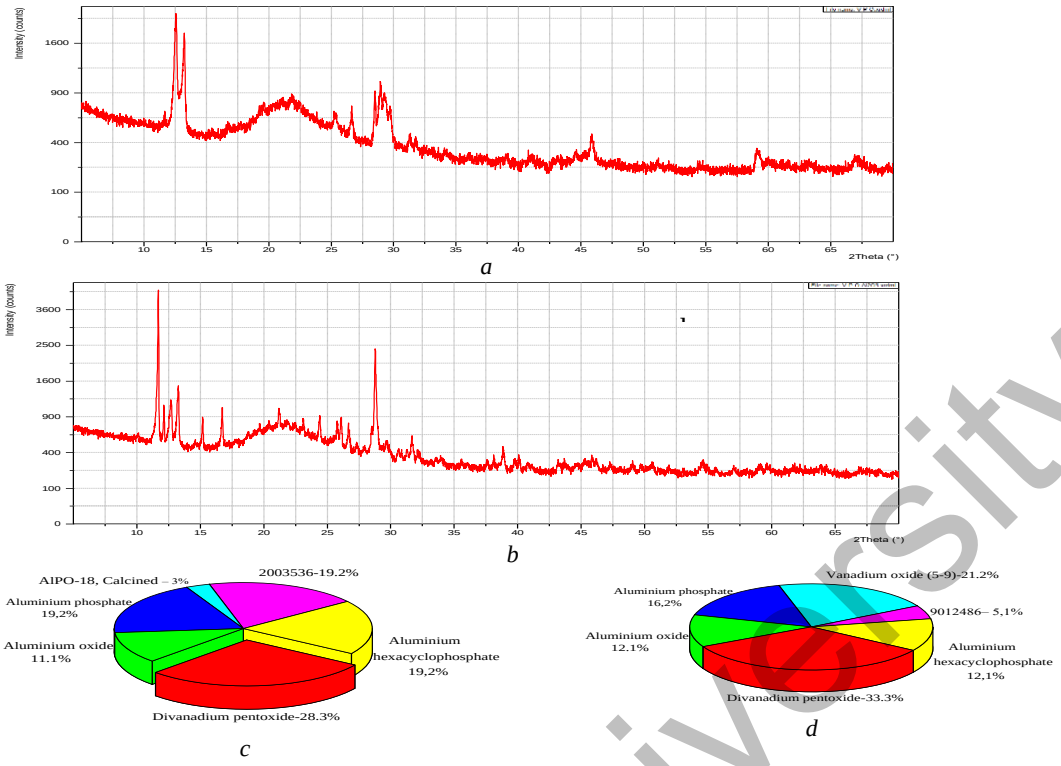


Figure 1. X-ray patterns of the *a*) V-P-O system and *b*) V-P-O/Al_2O_3catalyst; *c*, *d*) Phase distribution in the catalysts

It should be noted that the phase composition of the catalyst samples varies depending on the proportions of the active components that make them up. It has been determined that the catalytic systems consist of mixed phases and these phases are distributed as shown in Table 1.

Table 1

The formed phases in the V–P–Mo–O catalytic system

Mole ratio			Activation temperature, °C	Phases
V	Mo	P		
3	1	1	500	V_2MoO_8, $VO(PO_4)_2$, V_2O_5, P_2O_5, MoO_3
3	1	1	600	V_2MoO_8, $V_9Mo_6O_{40}$, $VO(PO_4)_2$, V_2O_5, P_2O_5
2	1	1	600	V_2MoO_8, $V_9Mo_6O_{40}$, $VO(PO_4)_2$, V_2O_5, P_2O_5
2	2	1	500	V_2MoO_8, $V_9Mo_6O_{40}$, $PVMoPO_4$, V_2O_5, P_2O_5
1	1	1	500	V_2MoO_8, $V_9Mo_6O_{40}$, $VOPO_4$, V_2O_5, P_2O_5, MoO_3
1	2	2	600	V_2MoO_8, $V_9Mo_6O_{40}$, V_2O_5, P_2O_5, MoO_3
1	1	2	600	V_2MoO_8, $V_9Mo_6O_{40}$, V_2O_5, P_2O_5, MoO_3
1	3	1	600	V_2MoO_8, $V_9Mo_6O_{40}$, $H_4PVMo_{11}O_{40}$, V_2O_5, P_2O_5

Thus, the formation of V_2MoO_8, $VOPO_4$, $V_9Mo_6O_{40}$ phases is mainly observed in the V:Mo:P=1:1:1 ratios in some mixing V–Mo–P–O catalyst samples. In these values of ratios (V:Mo:P=1:1:2, 1:2:2) $VOPO_4$ is not obtained, whereas other phases remain unchangeable. It should be noted that in this case V_2O_5, P_2O_5, MoO_3 phases are constantly observed. $VO(PO_4)_2$ phase formation together with V_2MoO_8, $V_9Mo_6O_{40}$ phases in V:Mo:P=1:1:2, 3:1:1 ratios, and $PVMoPO_4$ phase formation in V:Mo:P=2:2:1 ratio were observed. In the final case, it is necessary to note that the formation of V_2O_5, P_2O_5, MoO_3 phases were in sight, either. The activation temperature of the catalyst samples also affects the formation of these phases. When the activation temperature is 500–600 °C, that is, 50–150 °C higher than the reaction temperature, the formation of these phases is finished. At the same time, complete formation of phases is achieved during the oxidation process of chlorotoluenes. The change of initial components of catalyst samples also affects their degree of crystallization.

According to the surface characteristics of the VPO catalyst sample unsupported, supported and utilized in oxidation reaction, although the total surface area and radius of the pores rose from 12.025 m^2/g to 18.362 m^2/g and from 344 Å to 379 Å, respectively; the total volume of the pores in the supported VPO catalyst sample decreases. Considering the characteristic data of the surface after reaction, the earlier mentioned opinion — phase formation processes is over during oxidation process — has been confirmed. The increase of total surface area (23.355 m^2/g) and pore radius (379 Å) after the oxidation reaction can also be explained by the adsorption of unconverted chlorotoluenes on the surface, which can be confirmed by thermal analysis and post-processing IR spectra of the catalyst.

The surface characteristics data of the V–P–O sample have been achieved via special programming based on the BET equation and adsorption-desorption equations (Fig. 2).

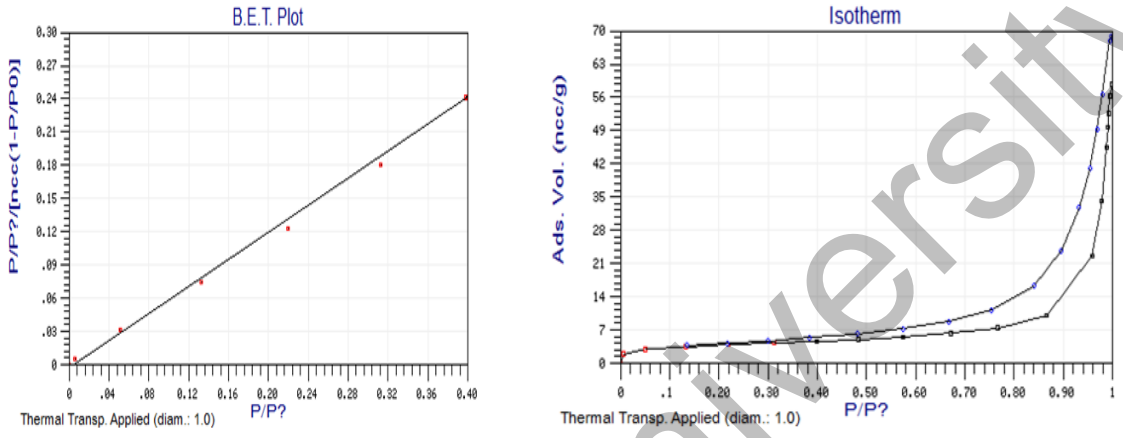


Figure 2. BET plot and adsorption isotherm of the VPO catalytic system

The corresponding surface data of the newly synthesized VPO catalysts, catalysts deposited on the support and catalysts applied in the oxidation process changes according to the following regularities are given in the Table 2.

Table 2

Surface data of the newly synthesized VPO, supported catalyst before and after oxidation

Catalyst simples	State of simples	Area of the surface, m^2/g	Radius, Å	Total volume, mL/g
V–P–O	Newly synthesized	12.025	344	0.710
V–P–O/SiO_2	Newly synthesized	18.362	379	0.072
V–P–O/SiO_2	After reaction	23.355	418	0.126

Thermogravimetric analysis revealed endothermic, exothermic effects and mass loss characteristics of catalytic systems. An endothermic effect corresponding to 140 °C is observed on the DTA curve of the investigated VPO/SiO_2 catalyst mixture before and after reaction (Fig. 3). Since the catalysts were analysed in their pure state, it can be assumed that the substances adsorbed on their surface are atmospheric water vapour and other low molecular weight compounds.

Strong and low-concentrated electron acceptor centers are formedin the unheated state of this sample, whereas strong and high-concentrated electron acceptor centers are formed after heating the sample and this is observed in the form of endothermic effects corresponding to the temperatures of 150, 480 and 550 °C on the DTG curve. When the catalyst is heated up to 400 °C, its activity decreases significantly, that is, very little physical adsorption and strong electron acceptor centers were detected after heating. In addition, in TA of the catalyst sample, a mass loss based on the destruction of the system is observed at a temperature above 700 °C, which is 200 °C higher than the reaction temperature and allows us to say that the catalysts are stable during the process and that no decomposition of their structure has occurred.

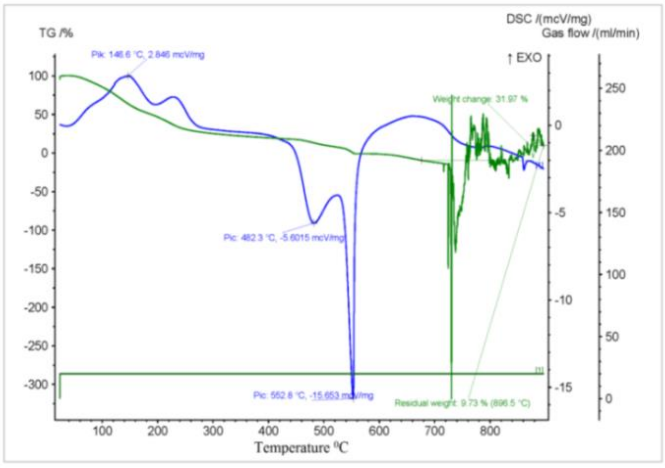


Figure 3. Thermogram obtained from the thermal analysis of the VPO/SiO_2 catalyst

Elemental analysis of the synthesized catalytic systems was also carried out. According to the obtained results, the compatibility between the theoretical calculations and the obtained practical data was tested, and also the correlation between parameters of the synthesized systems and theoretical calculations was determined (Table 3).

Table 3

Distribution of elements in the VPO system supported on SiO_2 (V:P=1:2)

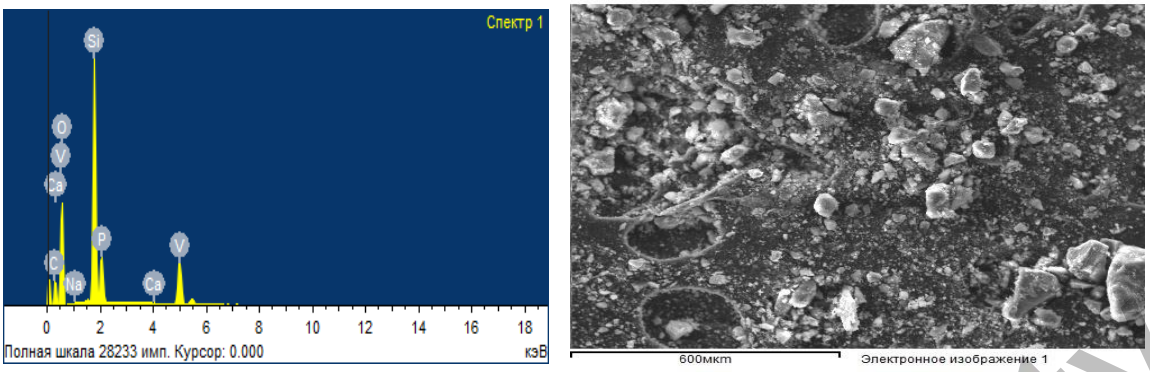
Element	Weight, %	Atom, %	Compound, %	Formula
Na	0.43	0.39	0.58	Na_2O
Si	28.62	21.26	61.23	SiO_2
P	9.59	6.46	21.97	P_2O_5
Ca	0.21	0.11	0.30	CaO
V	8.92	3.66	15.93	V_2O_5
O	52.23	68.12		
Total	100.00			

From the values of the distribution percentages of the components in the newly synthesized VPO/SiO_2 sample that the ratio of the components is V:P=1:2 (Table 3 and Fig. 4 *a*), the distribution of the elements included in the synthesized catalyst and the composition of which was calculated theoretically was confirmed experimentally. Thus, the distribution of vanadium, phosphorus and silicon in the VPO/SiO_2 sample is 3.66 %, 6.46 % and 21.26 %, respectively. In addition, similar experiments were carried out for other catalytic systems, and the distribution characteristics of the components in the catalyst samples were studied.

From the results of the elemental analysis, it is observed that the catalyst contains a small amount of sodium and calcium oxides; the probability of their effect on the course of the oxidation process is negligible.

The results obtained with a scanning electron microscope (Fig. 4 *b*) allow us to say that the surface of the catalyst is uneffected, complete, and rough. 10–12 nm particles were also observed in the images of the surface topology.

The catalyst samples were first heated at 373 K for 1 hour, then at 473 K for 2 hours, and then at 673 K in order to activate the obtained catalytic systems. At this stage, first, water and then the relevant gases are separated from the catalyst. The phase formation process in the catalyst sample heated up to 773 K is almost completed. The active phase formation of the catalysts ends after the influence of both O_2 and chlorotoluenes during the oxidation reaction. Thus, after thermal activation of the catalyst sample, these catalysts indicate lower activity after the first 4 hours in comparison to their activity after the next 2 hours in the oxidation of chlorotoluenes. It should be noted that the phases in the obtained catalysts are different depending on the ratio of the components taken for preparing the catalyst. The phase constitution of these catalyst samples was recorded, and the distribution of the phases present in the catalyst sample was clarified.



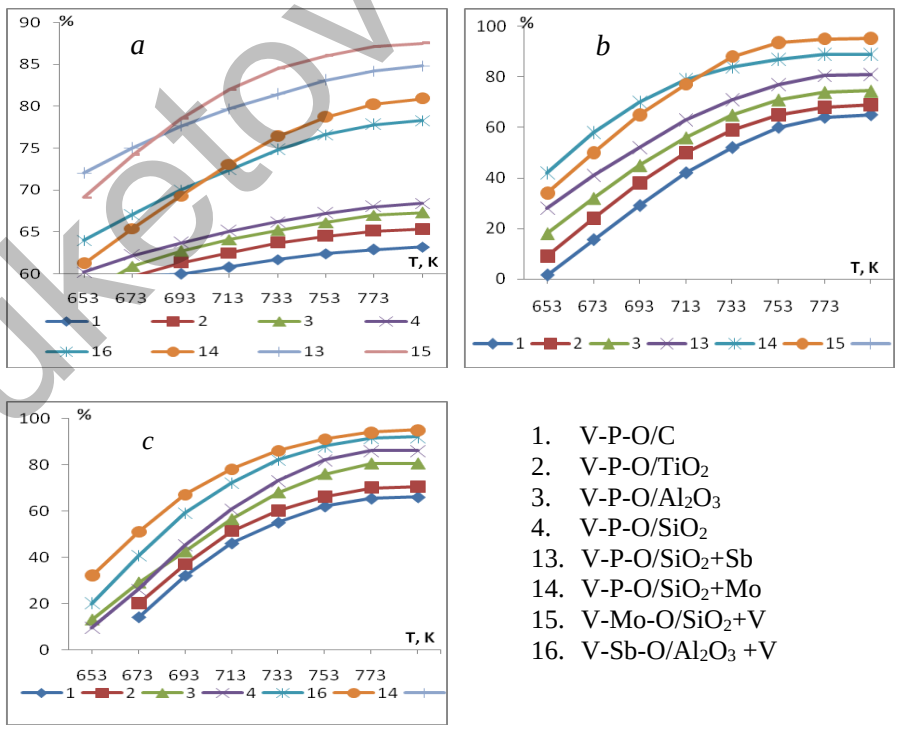
a *b*

Figure 4. Distribution spectrum of the elements that make up the VPO catalyst (*a*), Scanning electron microscope image of the VPO/SiO_2 catalytic system

Samples of synthesized active catalysts are as follows: 1. V–P–O/C, 2. V–P–O/TiO_2, 3. V–P–O/Al_2O_3, 4. V–P–O/SiO_2, 5. V–Mo–O/SiO_2, 6. V–Mo–O/Al_2O_3, 7. V–Sb–O/SiO_2, 8. V–Sb–O/Al_2O_3, 9. V–P–O/SiO_2+Mg, 10. V–Mo–O/Al_2O_3+Mg, 11. V–P–O/SiO_2+Zn, 12. V–Mo–O/SiO_2+Zn, 13. V–P–O/SiO_2+Sb, 14. V–P–O/SiO_2+Mo, 15. V–Mo–O/SiO_2+V, 16. V–Sb–O/Al_2O_3+V.

Monochlorotoluenes–2-chlorotoluene (2-*m*-ChT), 3-chlorotoluene (3-*m*-ChT), 4-chlorotoluene and dichlorotoluenes-2,4-dichlorotoluene (2,4-*d*-ChT), 2,3-dichlorotoluene (2,3-*d*-ChT), 2,5-dichlorotoluene (2,5-*d*-ChT), 3,4-dichlorotoluene (3,4-*d*-ChT) are mainly involved in the oxidation reaction. Initially, the temperature range, which is an essential factor of activity of catalytic syntheses in chlorotoluene oxidation process, is determined to find out the kinetic regularities of the process. The oxidation process of chlorotoluenes was carried out in open flow reactors with both stationary and fluidized layer of catalysts using the above-mentioned technique.

Oxidation of chlorotoluenes was carried out in the temperature range of 653–773K. The obtained results are shown in Figure 5.



1. V-P-O/C
2. V-P-O/TiO_2
3. V-P-O/Al_2O_3
4. V-P-O/SiO_2
13. V-P-O/SiO_2+Sb
14. V-P-O/SiO_2+Mo
15. V-Mo-O/SiO_2+V
16. V-Sb-O/Al_2O_3 +V

Figure 5. The effect of temperature on the catalytic activity in the oxidation reactions of *a*) 2-ChT, *b*) 3-ChT, *c*) 4-ChT

As is seen from the results, although the increase in temperature from 653 K to 713 K causes a significant raise in the activities of catalysts in the oxidation of monochlorotoluenes, this varies within the conversion range of 50–70 %. The activities of a number of catalyst samples V–P–O/C, V-P-O/TiO_2 are very low (40–50 %), while although the activities of some catalysts V–P–O/Al_2O_3, V–M–O/SiO_2, V–Mo–O/Al_2O_3 goes up slightly at relatively high temperature values (733–773 K), it does not exceed the 80–90 % limit. However, catalyst samples modified with some elements, such as Zn, V and Mo showed relatively high catalytic activity.

Although the modification of V–P–O/SiO_2, V–Mo–O/Al_2O_3 catalysts with Zn and Mg slightly increased the activity of the catalysts, additional modification of these catalysts with Mo, V and Sb gave better results. Thus, catalyst samples additionally modified with V and Mo(V–P–O/SiO_2+Mo, V–Mo–O/SiO_2+V, V–Sb–O/Al_2O_3+V) represented high activity even at low temperatures (673–713 K), the conversion of monochlorotoluenes was over 80 %, and these activities reached 90–95 % at the further temperature rise up to 733–773 K. The most optimal temperature was determined as 733–773 K.

The influence of the synthesis method of catalysts on their activity in the oxidation reaction of chlorotoluenes was also studied. The obtained results are given in the Table 3. As is seen from the table, the synthesis methods of catalysts do not affect the oxidation reaction of chlorotoluenes, so the conversion is 80–90 %, the yield of the main product — *m*-ChMA varies between 10–15 %, which can be considered insignificant.

The individual selective oxidation of mono- and dichlorotoluenes and the distribution of oxidation products were studied in presence of the catalytic systems that are active in the total oxidation process. Here, the oxidation of chlorotoluenes were studied at the optimal temperatures, contact times and optimal ratios of ChT:O_2 previously determined according to the results of the prior studies. The results of the selective oxidation of 4-ChT are given in Table 4.

The activities of the catalysts were determined by carrying out the oxidation process of chlorotoluenes in both stationary and fluidized open-flow reactors. Initially, the activities of a number of catalysts were found in the oxidation process of 4-chlorotoluene and 2,4-dichlorotoluene. The results are given in Table 4.

Table 4

Activities of the catalysts in the oxidation process of 4-*m*-ChT in the fluidized reactor

Selected components and oxides	Supporters	Reaction temperature, °C	Contact time, sec.	ChT:O_2 molar ratio	Conversion of the ChT, %	Yield of the products, %			
						ChBA	MA	*m*-ChMA	CO_2
V_2O_5	–	440	0.7	1:15	56	4	28	14	21
MoO_3	–	450	0.7	1:10	50	–	16	12	22
Sb_2O_3	–	420	0.6	1:10	84	–	10	6	18
P_2O_5	–	400	0.6	1:15	40	–	10	5	20
V_2O_5	SiO_2	440	0.7	1:15	60	5	18	15	22
MoO_3	SiO_2	450	0.7	1:10	55	–	15	14	23
P_2O_5	SiO_2	420	0.6	1:15	44	–	12	10	20
Sb_2O_3	SiO_2	420	0.6	1:10	38	–	8	4	18
V_2O_5	Al_2O_3	450	0.7	1:15	64	4	20	16	23
MoO_3	Al_2O_3	460	0.6	1:18	58	–	17	15	24
P_2O_5	Al_2O_3	420	0.7	1:10	47	–	14	12	20
Sb_2O_3	Al_2O_3	420	0.7	1:10	42	–	10	6	24
V_2O_5-P_2O_5	SiO_2	430	0.7	1:10	70	10	16	30	23
V_2O_5-P_2O_5	Al_2O_3	420	0.6	1:10	72	6	14	24	24
V_2O_5-MoO_3	SiO_2	430	0.6	1:15	70	5	15	25	22
V_2O_5-MoO_3	Al_2O_3	420	0.7	1:10	68	7	12	24	24
V_2O_5-Sb_2O_3	SiO_2	430	0.7	1:18	67	4	10	24	26
V_2O_5-Sb_2O_3	Al_2O_3	420	0.7	1:10	65	3	10	20	20
MoO_3- Sb_2O_3	SiO_2	430	0.6	1:10	63	–	8	18	26

The obtained results show that the conversion of 4-*m*-ChT varies between 40–84 % at 420–450 °C, 0.6–0.7 sec., and XT:O_2=1:15 molar ratio in the oxidation process carrying out in the presence of individual metal oxides without any supporter. However, chlorobenzaldehyde is obtained only up to 4 % in the pres-

ence of V_2O_5, while this is not observed in the presence of other oxides. At the same time, yields of MA and *m*-ChMA in the presence of V_2O_5 are 28 % and 14 %, respectively. But the value of this parameter decreases from MoO_3 to P_2O_5, namely from 16 % to 10 %, respectively. Even with this, it should be noted that the amount of CO_2, which is a product of deep oxidation, remains unchanged (20–22 %) in all cases. Studies conducted after depositing these oxides on the respective carriers Al_2O_3 and SiO_2 show that no major changes are observed. After deposition of V_2O_5 and P_2O_5 on SiO_2 supporter in a ratio of 1:2, both the yield of benzaldehydes and the yield of *m*-ChMA (30 %) increase in comparison with the previous ones. At this time, the yield of CO_2 is slightly reduced (23–24 %).

The effect of some technological parameters on the rate of the catalytic oxidation reactions of chlorotoluenes was studied with in wide temperature variation range (653–773 K), molar ratios of initial components 1:5–1:25 (chlorotoluene:oxygen), ratio of the active components of the catalyst 1:1–1:6, contact time of the reaction, concentrations of initial compounds and products of the reaction. It should be noted that among catalytic systems synthesized and utilized in the oxidation processes, V–P–O/SiO_2+Mo and V–Mo–O/SiO_2+V provide better results, so the experiments were basically carried out in the presence of these catalysts. First, the effect of contact time on the catalytic oxidation reactions of 4-chlorotoluene and 2,4-dichlorotoluene was studied, which resulted in conversion up to 84 % and total selectivity of about 65 %. The obtained results are given in Figure 6.

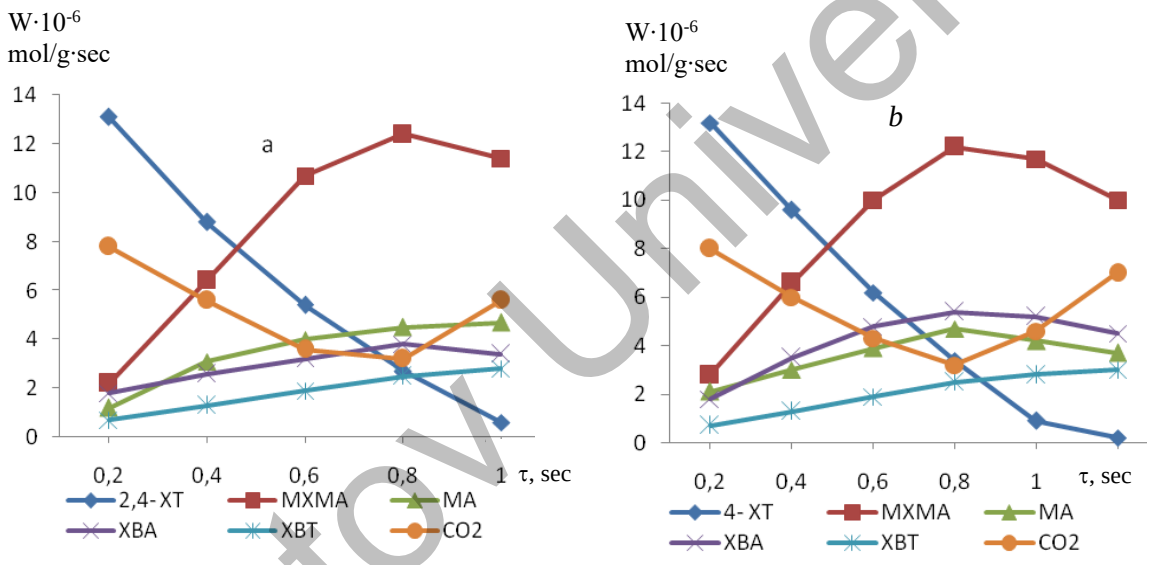


Figure 6. The effect of the contact time on the rate of the oxidation process of 4-ChT (*b*) and 2,4-ChT (*a*), T = 723 K, ChT:O_2=1:20

As can be seen in Figure 6, the consumption rate of both mono- and dichlorotoluene goes up with the contact time rise within 0.2–1.0 sec. When the contact time rises from 0.2 to 0.8 sec., the formation rate of benzaldehydes, maleic and chloromaleic anhydrides, which are oxidation products of both mono-and dichlorotoluene, increases and tends to decrease with the further raise. In addition to that, although the rate of the formation reaction of carbon dioxide (CO_2), a product of deep oxidation and the one obtained via parallel reaction during oxidation reactions decreases at first, however it grows rapidly after 0.8 seconds. After the contact time value of 0.8 seconds, the formation rates of maleic and chloromaleic anhydrides, as well as chlorobenzaldehyde, which are reaction products, decrease, this allows us to say that maleic and chlormaleic anhydrides undergo partial oxidation, chlorobenzaldehyde converts into chlorobenzoic acid (ChBA) through consecutive reaction and decomposes in the direction of deep oxidation. This is also confirmed by the increase in formation rates of CO_2 and ChBA.

These results indicate that the formation of the main products and by-products occurs on the surface of the catalyst by a parallel-consecutive reaction mechanism. This can be confirmed experimentally by establishing the dependence curve of the selectivities of the reaction products on the conversion of chlorotoluenes during the oxidation of chlorotoluenes at different contact times.

The dependence presented in Figure 7 confirms that targeted reaction products are obtained indeed from the competing oxidation reaction of chlorotoluenes, and then, CO_2 is obtained through the mechanism of the consecutive oxidation reaction of the anhydrides.

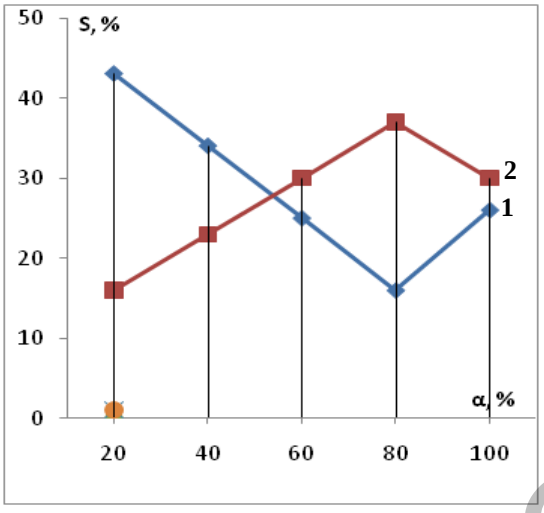


Figure 7. Dependence of selectivity (S) on conversion (α) in the oxidation reaction of 2,4-dichlorotoluene (2,4-*d*-ChT). *1* — m-ChMA, 2 — CO_2

All necessary calculations were performed using the software package "Optim Me" [19, 20].

Conclusions

The effect of the active components and modifiers (additives), promoters of the catalysts on their activities and selectivities were determined in the oxidation of chlorotoluenes and it was shown that the process goes mainly in the direction of obtaining *m*-ChMA and *d*-ChMA, if the ratio of the components included in the composition of catalyst is V:P=1:2, V:Mo=1:2. When the content of vanadium in the catalysts changes from 1:2 to 1:5 and higher, the yield of chlorobenzenedehyde in the oxidation process goes extensively. The addition of Sb to the catalyst leads to the growth of its service life and stability. In the study of the kinetic regularities of the oxidation of chlorotoluenes it was determined that the process occurs through the parallel-consecutive reaction mechanism in the presence of V–P–O/SiO_2 and V–Mo–O/Al_2O_3 catalysts in a wide range of technological parameters.

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