

## Deep Oxidation of Hydrocarbons on Polyoxide Nickel-Containing Catalysts

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The data on investigation of polyoxide Ni-Cu-Cr/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalysts on carriers with specified properties for deep oxidation of hydrocarbon - toluene, which has a strong toxic effect on living organism and flora, are given. The influence of technological parameters (temperature, space velocity, concentration of toluene in a mixture with air) on the completeness of the conversion of toluene (to CO<sub>2</sub> and H<sub>2</sub>O) on an effective polyoxide catalyst has been studied. It was shown that the synthesized polyoxide Ni-Cu-Cr catalyst supported on 2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> provides 98.8 % conversion of toluene to CO<sub>2</sub> in the oxidation reaction of toluene at a space velocity of 5×10<sup>3</sup> h<sup>-1</sup>, 723 - 773 K and the content of toluene 100 - 570 mg/m<sup>3</sup> in mixture with air.

### 1. Introduction

The problem of chemical safety and sanitary protection of air basin acquires particular relevance in connection with the increase in harmful emissions of industrial enterprises that have a strong toxic effect.

Cleaning of air polluted by exhaust gases of industrial enterprises and motor vehicles is the most actual direction of environmental protection. Harmful emissions of industrial enterprises (paint and varnish, furniture, cable, pharmaceutical, printing) and motor vehicles are the main polluters of cities. Many chemical compounds (toluene, xylene, styrene, phenol, tricresol, white spirit, etc.), which adversely affect the living organisms, are harmful toxic emissions of industrial enterprises (Zheksenbaeva et al., 2015).

Large amounts of harmful industrial emissions occur mainly in large cities, where their maximum permissible concentration (MPC) is much higher than normal. The content of harmful emissions above the MPC in industrial plants and in the atmosphere of air basin of cities cause negative impact on the living organism and lead to various diseases, thereby creating a threat to chemical safety of the environment (Brattoli et al., 2014).

Thermocatalytic purification of waste gases is becoming increasingly widespread among methods of cleaning harmful emissions of industrial enterprises (Popova et al., 2006). Catalysts based on platinum metals have high activity at low temperatures, durability, heat resistance and the ability to work stably at high space velocities. In the conditions of deficit and high cost of platinum group metals, the purpose of this work is to develop new approaches to the development of highly effective thermostable and poisonous polyoxide catalysts that do not contain noble metals that are stable for long periods of operation.

At present, the creation of gas cleaning catalysts that do not contain noble metals or contain them in small quantities is an important task. One promising way to solve this problem is the use of palladium catalysts with a low metal content, or catalysts based on mixed oxides.

Toluene was chosen as a model neutralization substance, as the main component of emissions from furniture, cable, shoe and other industries.

### 2. Experimental

#### 2.1 Catalysts preparation

Polyoxide catalysts were prepared by the capillary impregnation of cerium-modified alumina with mixed aqueous solutions of nitrate salts of metals by the moisture capacity of the carrier, followed by drying at 453 - 473 K (4 - 5 h) and calcination at 873 K (1 - 1.5 h) in air. Ball  $\theta$ -Al<sub>2</sub>O<sub>3</sub> (manufactured at the Institute of Catalysis of the SB

RAS, Novosibirsk) with a diameter of  $3 - 4 \times 10^{-3}$  m, specific surface of  $100 \text{ m}^2/\text{g}$ , bulk density of  $0.80 \text{ g/cm}^3$ , mechanical strength of 150 MPa and pore volume of  $0.48 \text{ cm}^3/\text{g}$  was used as a carrier for polyoxide catalysts (Tungatarova et al., 2014). To stabilize the structure and thermal stability,  $\theta\text{-Al}_2\text{O}_3$  was modified with cerium oxide, which forms a surface perovskite of the  $\text{CeAlO}_3$  type with aluminum oxide, stable up to 1,373 K.

## 2.2 Experimental

Deep oxidation of toluene was carried out on the PKU-2VD catalytic installation intended for testing of catalysts at pressures up to 3.4 MPa. Analysis of the initial mixture and reaction products were carried out using CHROMOS GC-1000 chromatograph with CHROMOS software. The temperature of thermal conductivity detector – 473 K, evaporator temperature – 553 K, column temperature - 313 K. The rate of carrier gas Ar - 10 mL/min. Catalytic activity of catalysts was determined in flow installation at deep oxidation of toluene in air at various temperatures (523 – 773 K), space velocities ( $5 - 15 \times 10^3 \text{ h}^{-1}$ ) and toluene concentration ( $320 \text{ mg/m}^3$ ) in the initial mixture.

The chromatographic peaks were calculated from the calibration curves plotted for the respective products using the "Chromos" software for pure substances (accurately measured quantities of a pure component or mixture of substances with known concentrations were injected into the chromatograph using a microsyringe). Based on the measured areas of peaks corresponding to the amount of the introduced substance, a calibration curve  $V = f(S)$  was constructed, where  $V$  - the amount of substance in ml,  $S$  - the area of peak expressed in  $\text{cm}^2$ . Concentrations of the obtained products were determined on the basis of the obtained calibration curves.

The phase composition of catalysts was determined by X-ray diffractometer DRON-4.7, Co anode, 25 kV, 25 mA,  $2\theta - 5 - 80^\circ$  (XRD). The BET specific surface area was determined by adsorption method using an Accusorb instrument (Micromeritics, United States) at the low temperature adsorption of  $\text{N}_2$ . The morphology, particle size, chemical composition of the Ni-Cu-Cr catalysts were investigated by transmission electron microscope EM-125K at 80,000 magnification by the replica method with extraction using a microdiffraction.

## 3. Results and discussion

### 3.1 Study of the effect of temperature on the activity of catalysts in the oxidation of toluene

The effect of temperature on the deep oxidation of toluene to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  on synthesized bimetallic and tricomponent Ni catalysts was investigated, Table 1. The activity of catalysts was studied at space velocity of  $5,000 \text{ h}^{-1}$  in the temperature range 523 - 773 K. It was determined that as the temperature rises from 523 to 773 K, the degree of toluene conversion increases on all catalyst compositions. It should be noted that the degree of toluene conversion stabilizes at a temperature of 723 K on all catalyst compositions.

Table 1: Effect of temperature on the deep oxidation of toluene to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  on synthesized Ni-Cu-Cr-containing catalysts at  $\text{GHSV} = 5 \times 10^3 \text{ h}^{-1}$ ;  $C_{\text{toluene}} = 320 \text{ mg/m}^3$

T, K	Degree of conversion of toluene, %			
	Ni-Cu/2 % Ce/ $\theta$ - $\text{Al}_2\text{O}_3$	Ni-Cr/2 % Ce/ $\theta$ - $\text{Al}_2\text{O}_3$	Cu-Cr/2 % Ce/ $\theta$ - $\text{Al}_2\text{O}_3$	Ni-Cu-Cr/2 % Ce/ $\theta$ - $\text{Al}_2\text{O}_3$
523	70.1	60.0	55.0	74.3
573	75.2	67.2	58.2	90.2
623	78.4	68.5	62.5	94.1
673	83.2	73.1	65.2	96.5
723	84.1	75.2	67.5	98.8
773	84.1	75.2	67.5	98.8

A further increase in temperature did not affect the conversion of toluene. Table 1 shows that the degree of conversion of toluene is lower on bimetallic composites for all the results of study compared to the three-component composition, when the temperature increases from 673 to 723 K. From these results, it follows that the maximum conversion of toluene occurs at Ni-Cu-Cr/2 % Ce/ $\theta$ - $\text{Al}_2\text{O}_3$  catalyst at 723 K (Zheksenbaeva et al., 2012).

The reaction of deep oxidation of model toluene on Ni-Cu-Cr/2 % Ce/ $\theta$ - $\text{Al}_2\text{O}_3$  catalyst modified with small additions (0.05 %) of noble metals (Pd and Pt) was studied.

Table 2 shows the dependence of the degree of conversion of toluene on the catalysts as a function of the reaction temperature from 523 to 773 K at  $\text{GHSV} = 5,000 \text{ h}^{-1}$  and  $C_{\text{toluene}} = 320 \text{ mg/m}^3$ . It was found that the degree of toluene conversion increases and reaches maximum of 99 % at 723 K on polyoxide Ni-Cu-Cr/2 % Ce/ $\theta$ - $\text{Al}_2\text{O}_3$  catalyst promoted by Pd as the temperature rises. A further increase in the reaction temperature to 773 K does not lead to a change in the activity of catalyst.

Table 2: Change in the degree of oxidation of toluene from the temperature and composition of catalysts at  $GHSV = 5,000 \text{ h}^{-1}$  and  $C_{\text{toluene}} = 320 \text{ mg/m}^3$

T, K	Degree of conversion of toluene, %		
	Ni-Cu-Cr/2 % Ce/ $\theta$ -Al <sub>2</sub> O <sub>3</sub>	Ni-Cu-Cr+Pd/2 % Ce/ $\theta$ -Al <sub>2</sub> O <sub>3</sub>	Ni-Cu-Cr+Pt/2 % Ce/ $\theta$ -Al <sub>2</sub> O <sub>3</sub>
523	74.3	81.0	83.2
573	90.2	92.5	95.3
623	94.1	97.0	98.4
673	96.5	98.2	99.0
723	98.8	99.0	100.0
773	98.8	99.0	100.0

Similar dependence of the activity on temperature was observed on the catalyst promoted by Pt. As can be seen from the table data, the conversion of toluene on the Pt-containing catalyst is higher than that of the polyoxide and Pd-containing catalysts and reaches 100 %.

Thus, the promotion by small additives (0.05 %) of Pd and Pt increases the activity of the synthesized three-component Ni-Cu-Cr/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst in the deep oxidation of toluene. It was found from the analysis of the obtained data, that the conversion of toluene on Ni-Cu-Cr/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst promoted by Pt reaches 100 % to the desired product at a temperature of 723 K.

### 3.2 Investigation of the effect of space velocity of the process on the efficiency of catalytic oxidation

The effect of varying the process space velocity on the degree of deep toluene conversion on the developed three-component Ni-Cu-Cr/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst was investigated. Experiments on deep oxidation were carried out in the temperature range 573 - 773 K and the concentration of toluene in the initial mixture with air equal to 320 mg/m<sup>3</sup>. From the data in Table 3 it can be seen that the degree of toluene conversion increases regardless of the change in space velocity with increase in the reaction temperature from 523 to 773 K. It was found that the highest conversion of toluene up to 98.8 % is achieved at the temperatures of 723 - 773 K and space velocity of 5,000 h<sup>-1</sup> as the space velocity increases from 5,000 to 15,000 h<sup>-1</sup>. The toluene conversion decreases to 93.5 and 89.3 % at higher space velocities to 10,000 and 15,000 h<sup>-1</sup> at temperature of 723 - 773 K, respectively.

Table 3: Study of the change in the degree of conversion of toluene in the deep oxidation of toluene on Ni-Cu-Cr/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst while varying temperature and space velocity

T, K	Space velocity, h <sup>-1</sup>		
	5,000	10,000	15,000
	$\alpha$ , %	$\alpha$ , %	$\alpha$ , %
523	73.7	81.0	82.1
573	89.5	85.7	83.8
623	94.7	90.5	85.7
673	97.5	91.5	89.3
723	98.5	93.5	89.3
773	98.5	95.2	89.3

Note - The concentration of toluene in the initial air mixture is 320 mg/m<sup>3</sup>

### 3.3 Determination of the influence of toluene concentration in gas-air mixture on the activity of catalysts

Influence of concentration of toluene in the initial mixture to the efficiency of its conversion on the polyoxide catalysts of various compositions were studied. Table 4 shows that increasing the concentration of toluene from 100 to 320 mg/m<sup>3</sup> in the initial mixture with air leads to a slight decrease in the degree of conversion of toluene on the two component Ni-Cu/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> and Cu-Cr/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalysts. A noticeable decrease in activity among two component oxide catalysts were found on the Ni-Cr-containing catalyst from 76.6 to 73.0 %. Ni-Cu-Cr/2 % Cr/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst was the most stable.

Thus, the optimal conditions of deep oxidation of toluene on oxide Ni-, Cu- and Cr-containing catalysts over 2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> were determined. Degree of conversion of toluene reaches 98.5 – 98.8 % on the Ni-Cu-Cr/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst at temperatures of 723 – 773 K,  $GHSV = 5 \times 10^3 \text{ h}^{-1}$  and the concentration of toluene in the initial mixture with air – 100 - 320 mg/m<sup>3</sup>.

Table 4: Effect the content of toluene in the initial mixture with air on degree of its conversion on the various catalysts

Catalysts	Concentration of toluene, mg/m <sup>3</sup>	
	100	320
Degree of conversion of toluene, %		
5 % Cu-Cr/2 % Ce/ $\theta$ -Al <sub>2</sub> O <sub>3</sub>	73.7	81.0
5 % Ni-Cr/2 % Ce/ $\theta$ -Al <sub>2</sub> O <sub>3</sub>	89.5	85.7
5 % Cu/2 % Ce/ $\theta$ -Al <sub>2</sub> O <sub>3</sub>	94.7	90.5
9 % Ni-Cu-Cr/2 % Ce/ $\theta$ -Al <sub>2</sub> O <sub>3</sub>	97.5	91.5

Note – T – 723 K; GHSV -  $5 \times 10^3 \text{ h}^{-1}$

From the obtained experimental data, it follows that the synthesized three-component catalyst exhibits a high activity in the deep oxidation of toluene.

### 3.4 The study of multicomponent oxide catalysts based on NiCuCr over 2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> by electron microscopy

The morphology and particle size of the developed catalysts were investigated using a transmission electron microscope EM-125K with an increase of 80,000 times by replicas with extraction using microdiffraction of electrons, Figure 1. It was found that single, double and triple metal oxides, whose particle size decreases from 50 - 80 Å (Ce/Al<sub>2</sub>O<sub>3</sub>) to 20 - 30 Å (Ni-Cu-Cr), are formed in the process of complicating the composition of copper three-component catalyst.

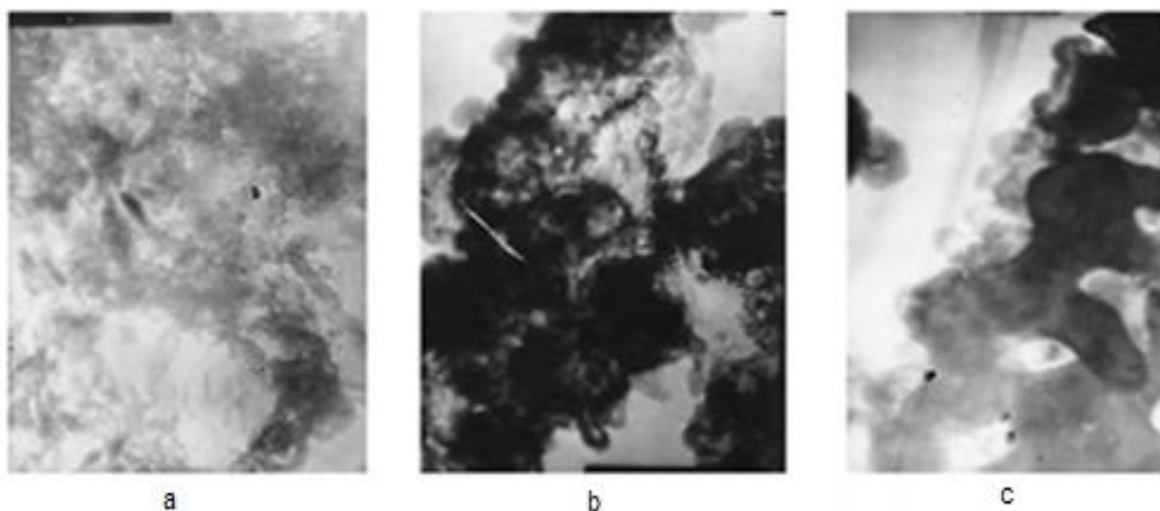


Figure 1: Electron microscopic photographs of the supported copper three-component catalyst: (a) Ni-Cu-Cr (873 K), (b) Ni-Cu-Cr + Pd (873 K), (c) Ni-Cu-Cr + Pd (1,473 K)

According to electron microscopy and microdiffraction of electrons follows that the catalysts contain mainly nanoparticles of oxides (20 - 100 Å) and their mixtures, as well as larger, dense particles of aluminates of the type AB<sub>2</sub>O<sub>4</sub>, ABO<sub>3</sub> of 200 - 300 Å size (Table 5) after heating at 873 K.

Also two types of particles: small oxides (60 – 150 Å) and larger aluminates are formed at introduction of Pt and Pd into Ni-Cu-Cr catalyst. Particles with a size greater than 1,000 Å are found in the case of promotion by Pd, especially when heated to 1,473 K. Most of the particles in the promotion by Pt are finely dispersed, which become larger after heating at 1,473 K to 200 – 500 Å due to the formation of aluminates and chromates. The relative content of large particles of metal aluminates in the Ni-Cu-Cr catalyst increases with the promotion by Pt and Pd and high-temperature heating.

According to electron microscopy and microdiffraction data, nanoparticles of metal oxides or their mixtures are formed in the initial oxide Ni-Cu-Cr catalyst after the decomposition of metal nitrates at 873 K. The process of interaction of elements with the  $\theta$ -Al<sub>2</sub>O<sub>3</sub> carrier with the formation of larger aluminates of copper and nickel of the type AB<sub>2</sub>O<sub>4</sub>, ABO<sub>3</sub> also occurs with an increase in temperature, despite its protection by cerium (CeAlO<sub>3</sub>) (Komashko et al., 2002).

Table 5: Electron microscopy data of polyoxide Ni-Cu-Cr catalysts on 2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>

Catalysts	T heating, K	Particle size, Å	Diffraction data
Ni <sub>1</sub> -Cu <sub>3</sub> -Cr <sub>0,1</sub>	873	20-30 20-100	NiCr <sub>2</sub> O <sub>4</sub> , CuCrO <sub>4</sub> , CuAl <sub>2</sub> O <sub>4</sub> , CuAlO <sub>4</sub> , NiAl <sub>2</sub> O <sub>4</sub> , CrO <sub>2</sub> , Cr <sub>2</sub> O <sub>3</sub> , CuAlO <sub>2</sub> , AlCu, NiCrO <sub>4</sub> , Cr <sub>2</sub> O <sub>3</sub>
	1,473	>200	CuAl <sub>2</sub> O <sub>4</sub> , NiAl <sub>2</sub> O <sub>4</sub> , CeAlO <sub>3</sub>
Ni <sub>1</sub> -Cu <sub>3</sub> -Cr <sub>0,1</sub> + Pd	873	100, 200-500 (flaky particles)	oxides of Cu, Ni, Cr, CeO <sub>2</sub> aluminates of Cu, Ni, CuCr <sub>2</sub> O <sub>4</sub> , Pd, PdO, Ce <sub>2</sub> O <sub>3</sub> , CrO <sub>2</sub> , NiCrO <sub>3</sub> , CuAl <sub>2</sub> O <sub>4</sub> , CuCr <sub>2</sub> O <sub>4</sub> ,
	1473	>1,000	NiCrO <sub>3</sub> , CeAlO <sub>3</sub> , oxides of Cu, Ni, Cr, NiAl <sub>26</sub> O <sub>42</sub> Cu <sub>2</sub> O, Ni <sub>2</sub> O
Ni <sub>1</sub> -Cu <sub>3</sub> -Cr <sub>0,1</sub> + Pt	873	60-150	oxides of Cu, Ni, Cr, Pt <sup>o</sup> Cu <sub>2</sub> O, Ni <sub>2</sub> O, PtO, NiAl <sub>2</sub> O <sub>3</sub>
	1,473	200-500 (dispersing and enlarging)	CuAl <sub>2</sub> O <sub>4</sub> , CrO <sub>4</sub> , Cr <sub>2</sub> O <sub>3</sub> , Ni <sub>2</sub> O Cu <sub>2</sub> O, Pt <sup>o</sup> , NiCrO <sub>4</sub> , Ni <sub>2</sub> O

### 3.5 Study of polyoxide catalysts based on Ni, Cu and Cr oxides on 2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> by XRD method

The developed Ni-Cu-Cr/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst was investigated by X-ray diffraction analysis (XRD). The phase composition of the catalysts was determined on a DRON-4-7 X-ray diffractometer, Co-anode, 25 kV, 25 mA, 2 $\theta$  - 5-80°C.

Table 6 shows the results of determining the phase composition of the initial 2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> and Ni-Cu-Cr on 2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalysts after preparation (T heating = 873 K, 1 h) and prolonged heating (5 h) in air with an increase in temperature from 873 K to 1,473 K.

Table 6: X-ray phase analysis of polyoxide Ni<sub>1</sub>-Cu<sub>3</sub>-Cr<sub>0,1</sub> catalysts supported on 2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub>

Catalyst	Promoter, %	T heating, K	CeO <sub>2</sub> , 1,91 Å	$\alpha$ -Al <sub>2</sub> O <sub>3</sub> , 1,74 Å	$\theta$ -Al <sub>2</sub> O <sub>3</sub> , 2,31 Å	NiAl <sub>2</sub> O <sub>4</sub> , CuAl <sub>2</sub> O <sub>4</sub> , 1,43 Å	Less intensive phases	
Ni-Cu-Cr		873	13	37	10		CuO (2,51; 2,31; 1,85), NiO (2,08; 2,42; 1,48)	
		1,273	58	158	5	90		
		1,473	30	120	3	105		
	0,3 Pt	873	10	9	22		CuO, Al <sub>2</sub> O <sub>3</sub> (2,12), NiO (2,42)	
0,1 Pt	873	14	20			CuO, Al <sub>2</sub> O <sub>3</sub> (2,12), Ce <sub>6</sub> O <sub>11</sub> , Cr <sub>5</sub> O <sub>12</sub> (3,57)		
0,1 Pt	1,073	26	20	10	10		CuO, NiO, Ce <sub>6</sub> O <sub>11</sub> , Al <sub>2</sub> O <sub>3</sub>	
0,3 Pt	1,473	52	166	5	70			
Ni-Cu-Cr	0,05 Pd	873	20	13	7	7		CuO, Ce <sub>6</sub> O <sub>11</sub> , Al <sub>2</sub> O <sub>3</sub> (2,12)
	0,05 Pd	1,273	45	148	2	55		Pd (2,25)
	0,05 Pd	1,473	60	177	5	105		NiAl <sub>10</sub> O <sub>16</sub> (1,99)

Reflexes from  $\theta$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub> (quantitative evaluation was carried out on reflections of 2.31 Å, 1.74 Å, 1.91 Å) are present both in 2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> and in the carrier. The intensity of the CeO<sub>2</sub> reflexes increases slightly as the Ce content in the catalyst increases and, especially after heating, successively at 873, 1,073, 1,273, 1,373, and 1,473 K. This indicates that the crystallization of amorphous CeO<sub>2</sub> occurs as a result of heating. The same process is typical for supported on 2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalysts, but to different degrees.

Intensive reflexes from CuO and less intense from NiO, in addition to the phases of CeO<sub>2</sub> and  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, are observed in the X-ray diffraction patterns of Ni-Cu-Cr/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst heated at 873 K. Not only the crystallization of CeO<sub>2</sub>, but also a sharp increase in the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> content, starting from 1,273 K, occurs as the catalyst warms up. This indicates that the process of interaction of CuO, and also NiO with  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, followed by the destruction of spinel to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and oxides occurs. A significant decrease in the total surface area of catalysts is due to this process during heating. Promotion of the Ni-Cu-Cr catalyst by Pt and Pd also contributes to phase transformations in the catalyst during heating. Weak reflexes from NiO, Ce<sub>6</sub>O<sub>11</sub>, and also NiAl<sub>10</sub>O<sub>16</sub> are present in the X-ray diffraction pattern, in addition to crystalline CeO<sub>2</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, CuO, and Ni(Cu)Al<sub>2</sub>O<sub>4</sub>. (Grigor'eva et al., 2002).

The use of X-ray phase analysis to study of polyoxide catalysts supported on 2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> showed that the active components in the initial catalysts are mainly in the X-ray amorphous state. Part of Ni and Cu in the Ni-Cu-Cr catalyst is represented by Ni and Cu oxides, especially at the promotion by platinum. Ni-Cu-Cr catalyst heated up to 1,473 K undergoes significant changes in the phase composition: Cu oxide interacts with the carrier to form CuAl<sub>2</sub>O<sub>4</sub>, and due to the decomposition of the latter, the amount of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> increases.

#### 4. Conclusions

As a result of the obtained data, it was found that among the synthesized Ni-, Cu-, Cr-containing catalysts supported on alumina modified with the addition of Ce, the highest degree of toluene conversion (up to 98.8 %) is observed on a three-component Ni-Cu-Cr/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst at space velocity of 5,000 h<sup>-1</sup> and a temperature of 723 - 773 K. It was determined that the promotion by small amount (0.05 %) of Pd and Pt of the synthesized polyoxide three-component Ni-Cu-Cr/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst increases the conversion of toluene in deep oxidation to CO<sub>2</sub> and H<sub>2</sub>O to 100 %. By X-ray diffraction and electron microscopy was determined the presence of CeO<sub>2</sub> crystals and X-ray amorphous clusters ( $d = 20 - 100 \text{ \AA}$ ) of metal oxides of variable valence NiO and CuO, and also solid metal solutions CuO(NiO) on a surface of Ni-Cu-Cr/2 % Ce/ $\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst calcined at 873 K. When the Ni-Cu-Cr catalyst is heated above 1,273 K in air, phase transformations take place: metal oxides interact with alumina to form aluminates of the MeAl<sub>2</sub>O<sub>4</sub> type with  $d = 200 - 1,000 \text{ \AA}$  with simultaneous decrease in the specific surface area.

#### Acknowledgments

The work was supported by the Ministry of Education and Science of the Republic of Kazakhstan (Grant No 0246/GF4).

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