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INVESTIGATION OF Ni-CONTAINING CATALYSTS FOR THE PURIFICATION OF EXHAUST GASES

Abstract. Results of the development of multicomponent oxide catalysts for the purification of exhaust gases based on Ni, Cu, and Cr supported on 2% Ce/ θ -Al₂O₃ by varying the concentration of the active phase of catalyst are presented in paper. It was found that the highest degree of toluene conversion (up to 98.8 %) is observed on the three-component Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ catalyst with optimal metal ratio Ni : Cu : Cr = 1.0 : 3.0 : 0.1 at GHSV = 5410³ h⁻¹ and a temperature of 723 - 773 K. The presence of CeO₂ crystals, X-ray amorphous clusters ($d = 20 - 100$ E) of variable valence metal oxides NiO and CuO as well as solid metal solutions CuO (NiO) and aluminates was detected on the surface of optimum catalyst calcined at 873 K using XRD and transition electron microscopy methods. Preparation of polyoxide supported catalysts as well as study the influence of catalyst composition and modified additives on deep oxidation of toluene - a major component of toxic organic gaseous industry emissions, is the goal of research.

Key words: catalytic oxidation, toluene, purification, nickel, copper.

Introduction. The problem of chemical safety and sanitary air protection is particularly relevant due to the increase of harmful emissions of industrial enterprises, which have a strong toxic effect. Many chemical compounds (toluene, xylene, styrene, phenol, tricresol, mineral spirits, CO, etc.), which negatively affect the living organisms and flora are harmful toxic emissions from industrial plants. Under the Paris agreement, adopted on December 12, 2015 and signed on April 22, 2016, in addition to the United Nations Framework Convention on Climate Change (UNFCCC), developed countries and countries with economies in transition have to reduce or stabilize greenhouse gas emissions [1]. The content of harmful emissions above the MPC in industrial workshops and atmospheric air in the cities cause a negative impact on living organisms and lead to various diseases thereby creates a threat to the safety of the environment [2]. Toluene, xylene and ethyl-benzene are major part of the solvents used in various industries, which are present in gaseous emissions [3]. Toxic and adverse effect of harmful emissions on a living organism can be traced on the example of toluene - a major component of toxic organic gaseous emissions that are present in the emissions of furniture, paint, cable, printing and other industries. For example, the inhalation of toluene with a concentration of 250 mg m⁻³ for 2 h leads to a decrease in heart rate, disturbance of speech, movement coordination [4]. Prolonged inhalation of toluene, which is present in the composition of glue, varnishes, paints, etc., causes neurotoxic deviations that lead to clinical consequences - hallucinations, somnolence, suicide attempts, visual disturbances and seizures.

From the literature data [5] on the methods and apparatuses for neutralization of toxic emissions follows that deep catalytic oxidation is the most economical way for cleaning of gases from the emissions of complex composition [6]. Typically, the catalysts based on noble metals (Pt, Pd) [7], which have high

activity (95-100 %) in complete oxidation of organic substances [8], are used mainly for cleaning of waste gas of industrial enterprises [9]. Catalysts based on Pt group metals have high activity at low temperatures, durability, heat resistance and ability to operate stably at high space velocities. Conditions of deficit and high cost of platinum group metals lead to the need to develop new approaches to the creation of highly effective polyoxide catalysts that do not contain noble metals capable exhibit a high thermal stability and poison-resistance and sustainable in the long term operation [10-15]. Creation of catalysts for gas purification, which do not contain noble metals or contain them in small amounts [16], is an important goal. In this context, the development of high-performance polyoxide catalysts, which do not contain precious metals, and technology for deep oxidation of toxic organic gaseous emissions from industry are relevant.

Experimental. Purification of exhaust gases from harmful organic impurities, in particular from toluene, was carried out on a flow installation, the implementation conditions of which are close to real conditions.

The granulated θ -Al₂O₃ ($S = 100 \text{ m}^2 \text{ g}^{-1}$, particle size between 40 and 50 μm) modified by Ce, which forms resistant surface CeAlO₃ perovskite up to 1,373 K was used as a carrier. Polyoxide catalysts were prepared by capillary impregnation of alumina modified with cerium by mixed aqueous solution of Ni, Cu and Cr nitrates by incipient wetness, followed by drying at 453 - 473 K (4 - 5 h) and calcination at 873 K (1 - 1.5 h) in air. The prepared oxide catalysts have been promoted with Pt and Pd (0.05%) to improve the activity and thermal stability.

Deep oxidation of toluene was carried out on the flow type PKU-2VD catalytic installation intended for testing of catalysts at pressures from atmospheric pressure up to 3.4 MPa in tubular reactor with fixed catalyst bed. Catalytic activity of catalysts was determined in flow installation at deep oxidation of toluene in air at various temperatures (523 - 773 K), space velocities ($5 - 15 \cdot 10^3 \text{ h}^{-1}$) and toluene concentration (320 mg m^{-3}) in the initial mixture.

Analysis of the initial mixture and reaction products were carried out using CHROMOS GC-1000 chromatograph. The rate of carrier gas (Ar) - 10 ml min^{-1} .

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 morphology, particle size and chemical composition of the Ni-Cu-Cr catalysts were investigated using transmission electron microscope EM-125K at 80,000 times magnification by the replica method with extraction using microdiffraction (TEM). The surface of catalysts was determined by the BET method on the low temperature N₂ adsorption using the Accusorb apparatus (Micromeritics, USA).

Determination of the amount of adsorbed oxygen by catalysts, its characteristics, as well as the ability to interact with a reducing agent (H₂) were carried out by methods of temperature-programmed desorption of oxygen (TPD) and temperature-programmed reduction (TPR). Temperature-programmed reduction of catalysts after the formation in air at 873 K were carried out by passing a mixture of H₂ (10%) and He (90%) at 20 ml min^{-1} and the temperature rises at speeds of 8 K min^{-1} from 293 to 1,173 K (at 1,173 K temperature was stabilized).

Results and discussion. Investigation of the activity of polyoxide catalysts in the reaction of deep oxidation of toluene at 723 K and space velocity $5 \cdot 10^3 \text{ h}^{-1}$ is presented. The conversion of toluene increased with the complexity of the composition of catalysts. The lowest 57.0 % degree of toluene oxidation was observed on the 5% Ni/2% Ce/ θ -Al₂O₃ catalyst, and the greatest 98.5% degree was observed on the three-component 9% Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ catalyst. The following series by activity in the reaction of deep oxidation of toluene was determined: Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ (98.5%) > Ni-Cu-Cr/ θ -Al₂O₃ (92.0%) > Ni-Cu/2% Ce/ θ -Al₂O₃ (84.0%) > Ni-Cr/2% Ce/ θ -Al₂O₃ (75.0%) > Ni/2% Ce/ θ -Al₂O₃ (57.0%). The largest conversion of toluene is observed on three-component Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ catalyst with an optimal ratio of metals Ni: Cu : Cr = 1.0 : 3.0 : 0.1 at $T = 723 \text{ K}$. The degree of toluene oxidation reduces from 98.5 to 89.3% with the increase of space velocity from $5 \cdot 10^3$ to $15 \cdot 10^3 \text{ h}^{-1}$, respectively.

Increasing the concentration of toluene from 100 to 320 mg m^{-3} 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/ θ -Al₂O₃ and Cu-Cr/2% Ce/ θ -Al₂O₃ catalysts. A noticeable decrease in activity between two component oxide catalysts was found on the Ni-Cr-containing catalyst from 76.6 to 73.0%. Ni-Cu-Cr/2% Cr/ θ -Al₂O₃ 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/ θ -Al₂O₃ were determined. Degree of conversion of toluene reaches 98.5 – 98.8% on the Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ catalyst at temperatures of 723 - 773 K, GHSV - 5410³ h⁻¹ and the concentration of toluene in the initial mixture with air – 100 - 320 mg m⁻³.

The intensive reflections from CuO and less intensive from NiO, CeO₂, and θ -Al₂O₃ are observed in roentgenograms of the Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ catalyst heated at 873 K. Not only CeO₂ crystallization, but a sharp increase in the content of α -Al₂O₃ starting from 1,273 K is a result of heating of the Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ catalyst. Significant reduction of the total surface area of catalysts is due to heating. CeO₂ crystallization occurs to a lesser extent due to the small (2%) of Ce content (in carrier only). According to XRD the presence of CeO₂ crystals and X-ray amorphous clusters with diameters from 20 to 100 E, metal oxides of variable valence NiO, CuO, and solid solutions of metals CuO (NiO) is fixed on the surface of carrier in the process of catalyst synthesis after heating at 873 K. Phase transformations occur in the Ni-Cu-Cr catalyst upon heating in air above 1,273 K. Metal oxides react with alumina to form the Me-Al₂O₄ type aluminates with diameter from 200 to 1,000 E and the surface decreases sharply to 2 - 5 m². Reflexes from the θ -Al₂O₃, α -Al₂O₃, and CeO₂ are presented in the 2% Ce/ θ -Al₂O₃, as well as in the carrier (quantification was performed by reflections 2.31 E, 1.74 E, 1.91 E, respectively). The intensity of CeO₂ reflexes increases slightly with increasing the Ce content in catalyst, and especially after the heating consistently at 873, 1,073, 1,273, 1,373 and 1,473 K. This indicates that crystallization of the amorphous cerium oxides happens as a result of heating. The same process is characteristic for supported on the 2% Ce/ θ -Al₂O₃ catalysts, but to different degrees.

Thus, the use of X-ray diffraction analysis to study of polyoxide catalysts supported on 2% Ce/ θ -Al₂O₃ showed that the active components are mainly in amorphous state in the initial catalysts; part of Ni and Cu is represented by Ni and Cu oxides [17].

The morphology and particle size of the developed catalysts were examined by transmission electron microscope on the EM-125K at magnification 80,000 times by the replica method with extraction using electron microdiffraction. It was found that single, double and triple metal oxides, the particle size of which are decreased from 50-80 E (Ce/Al₂O₃) to 20-30 E (Ni-Cu-Cr) are formed at complication the composition of three-component catalyst. The nanoparticles of metal oxides or their mixtures are formed after decomposition of nitrates of initial oxide Ni-Cu-Cr catalyst at 873 K according to electron microscopy and microdiffraction. Interaction of elements with θ -Al₂O₃ carrier with formation of larger copper and nickel aluminates of the AB₂O₄ and ABO₃ type occurs when the temperature rises [18].

Figure 1 shows the spectra of thermal desorption of oxygen from the oxide Ni-Cu-Cr/ θ -Al₂O₃ after oxygen adsorption at 873 K. It is seen that the amount of oxygen released upon heating to 1,173 K (stabilizing temperature) increases with the complexity of the composition of mixed catalyst. Desorption curve has bends at 773 K and 923 K as well as maximum at 1,023 K, which is caused by desorption of the adsorbed oxygen (673 – 873 K) and decomposition (873-1,073 K) of copper and nickel oxides (up to Cu₂O, Ni₂O) and then mixed oxides (> 1,070 K).

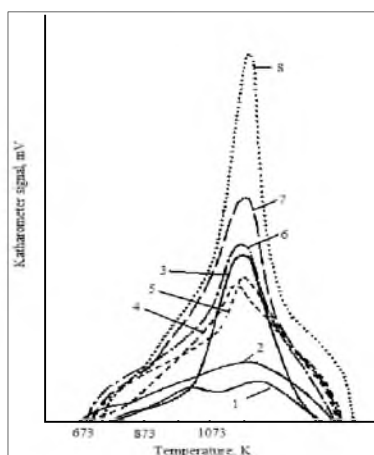


Figure 1 – Thermal desorption of oxygen from the catalysts on Al₂O₃ after heating in air:
 1-5% Ni, 2-5% Cu, 3-5% Cr, 4-5% (Ni + Cr), 5-5% (Cu + Cr), 6-8-10% Ni-Cu-Cr at varying the deposition methods of catalysts:
 6 - NH₄HCO₃, 7 - Al(NO₃)₃, 8 - NH₄HCO₃ + Al(NO₃)₃, T – 873 K, 1 h

The total amount of released oxygen (9.7 mmol from the 1.0 g of active phase) exceeds the probable sorption at each of oxides. This is obviously connected with the dissolving of oxides of superstoichiometric oxygen in formed solid solutions, which are released at lower temperatures [19]. The total amount of released oxygen (mainly due to weak adsorbed oxygen) from the Ni-Cu-Cr catalyst depends on the conditions of preparation of mixed carbonates and their decomposition. It is increased by 2 times when using $\text{NH}_4\text{HCO}_3 + \text{Al}(\text{NO}_3)_3$ in the precipitation of mixture.

Calculation of activation energy release of oxygen from the catalyst showed that it is 88 - 89 kJ/mol. Desorption energy from single copper oxides is 128 kJ/mol; from nickel oxides - 120 kJ/mol and from mixed oxides - 140 - 144 kJ/mol.

Heating of Ni-Cu-Cr/2% Ce/ θ - Al_2O_3 catalyst at 1,473 K sharply reduces the release of oxygen in the area of decomposition of metal oxides for the initial and promoted contacts (Figure 2). The area of adsorbed oxygen completely disappears in the spectrum of Ni-Cu-Cr and Ni-Cu-Cr + Pt catalysts. The observed phenomenon can be explained by the fact that most of the metal oxides reacts with the carrier to form large (200 - 1,000 Å) Ni(Cu) Al_2O_4 aluminates (XRD and TEM), because of which the total surface area of contacts is reduced from 60 to 5 m² g⁻¹ [20].

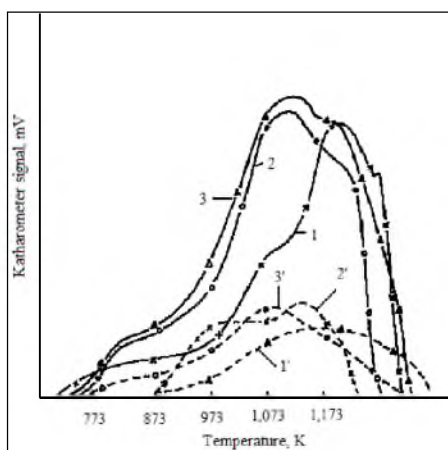


Figure 2 – Thermal desorption of oxygen from the Ni-Cu-Cr/2 % Ce/ Al_2O_3 catalyst heated in oxygen and promoted with Pd and Pt: 1 - Ni-Cu-Cr/2 % Ce/ Al_2O_3 , 2 - Ni-Cu-Cr/2 % Ce/ Al_2O_3 + Pd, 3 - Ni-Cu-Cr/2 % Ce/ Al_2O_3 + Pt. 1¹, 2¹, 3¹ - catalysts after heating at 1,473 K, T – 873 K

The study of temperature-programmed reduction of Ni-Cu-Cr/2% Ce/ θ - Al_2O_3 catalysts allowed to make one more step in understanding of reduction mechanism and elimination of oxygen from oxides, and to assess the ability of catalyst to absorb oxygen from gas phase.

Figure 3a shows that the TPR curve has four hydrogen absorption peaks: $T_1 = 523$ K, $T_2 = 573$ K, $T_3 = 673$ K and $T_4 = 1,073$ K corresponding to reduction of CuO (T_1), mixed oxides CuO-NiO (T_2), NiO (T_3) and formed partially Ni or Cu aluminates.

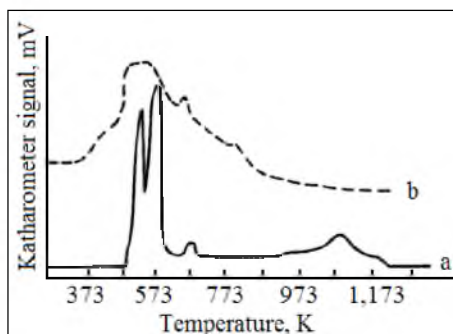


Figure 3 – TPR and TPO spectra of the initial Ni-Cu-Cr/Ce/ θ - Al_2O_3 catalyst: a - TPR of the initial catalyst, b - TPO after TPR up to 1,225 K

Temperature-programmed oxidation (TPO) of catalyst after its reduction up to 1,225 K (figure 3b) showed that oxygen is adsorbed easily, starting from 357 – 373 K, as a broad peak with $T_m^1 = 523$ K, $T_m^2 = 673$ K and $T_m^3 = 800 - 810$ K, which corresponds to adsorption of it on surface (T_m^1) and formation of Ni and Cu oxides. Ni-Cu-Cr/Ce/ θ -Al₂O₃ catalyst has undergone profound changes in the phase composition after heat treatment at 1,473 K 5 h (Figure 4a).

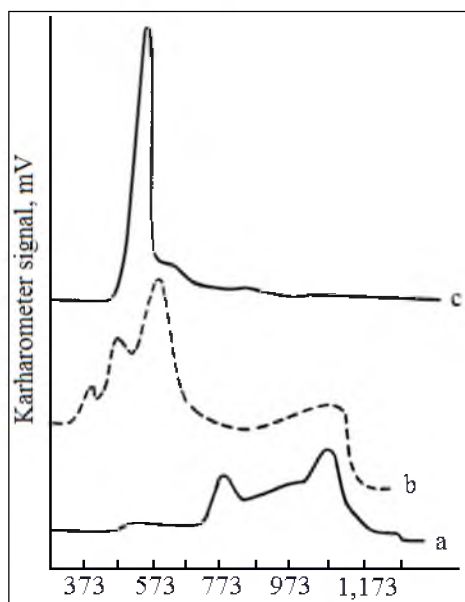


Figure 4 - TPR and TPO spectra of the Ni-Cu-Cr/Ce/ θ -Al₂O₃ catalyst:
 a - TPR of the initial catalyst, b - TPO of catalyst reduced up to 1,223 K,
 c - TPR of catalyst after treatment in oxygen to 973 K, T - 1,473 K, 5 h

Weak bending of curve at 473 K is available in TPR spectrum. The main absorption of H₂ occurs at $T_m = 773$ and 1,073 K when Cu (Ni) aluminates are reduced. Cu(Ni)Al₂O₄ crystals (2,42 reflex) is also fixed according to XRD. If the reduction temperature of catalyst reaches 1,223 K, the adsorption of oxygen in the initial Ni-Cu-Cr catalyst is carried out at a temperature above than 373 K (figure 4b).

Subsequent temperature-programmed reduction of catalyst indicates on absorption of H₂ only as a single peak (Figure 4c). This indicates that a mixture of Ni(Cu) oxides, which are reduced at 523 K, is synthesized from aluminates.

Thus, Ni-Cu-Cr catalyst is a solid solution of copper and nickel oxides with chromium, included in it, according to the TPD and TPR results. Superstoichiometric surface oxygen with $E_{des} = 88 - 89$ kJ mol⁻¹, which reacts easily with reducing agents is adsorbed onto its surface. TPD curves and TPO data indicate on its presence in catalyst. Besides mixed oxides the less active Ni and Co aluminates are formed in the oxidation process at high temperatures in catalyst in an oxidizing atmosphere.

Conclusion. As a result of studies, it was found that the highest degree of toluene conversion (to 98.8 %) is observed on three-component Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ catalyst with optimal ratio Ni : Cu : Cr = 1.0 : 3.0 : 0.1 at space velocity of 5410³ h⁻¹ and temperature 723 - 773 K. The binding energy of oxygen with surface and its reactivity on polyoxide catalysts were determined by the TPD, TPO and TPR methods. It was shown that formed Ni and Cu aluminates can be reduced to the initial oxides or their mixtures under the influence of H₂ at 973 - 1,223 K. Again, oxygen adsorption on Ni-Cu-Cr catalysts after decomposition of oxides occurs at low temperature (325 K). This point to high reactivity of adsorbed O₂⁻, O⁻, and lattice oxygen of dispersed oxides, as well as mixtures thereof, and its ability to easy reactivation.

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ШЫҒАРЫЛҒАН ҒАЗДАРДЫ ТАЗАРТУ ҮШІН Ni-ҚҰРАМДЫ КАТАЛИЗАТОРЛАРДЫ ЗЕРТТЕУ

Аннотация. Химиялық қауіпсіздік және ауаны санитарлық қорғауда қатты уытты әсер ететін өнеркәсіптік кәсіпорындардан шығарылатын зиянды қалдықтың артуы өзекті мәселе болып саналады. Өндірістік кәсіпорындардан шығатын зиянды улы қалдықтар, яғни көптеген химиялық қосылыстар (толуол, ксилол, стирол, фенол, трикрезол, минералды спирттер, СО және т.б.) тірі организмдер мен флораға теріс әсер тигізеді. Климаттың өзгеруі жөніндегі 2015 жылы 12 желтоқсанда қабылданған Париж келісіміне және 2016 жылы 22 сәуірде қол қойылған Біріккен Ұлттар Ұйымының конвенциясына сәйкес дамыған және экономикасы дамушы елдерде парниктік газдардың шығындысын азайтып, тұрақтандыру қажет. Өнеркәсіптік цехтардан шығарылған зиянды газдардың құрамы қаладағы атмосфералық ауада шекті рұқсат етілген концентрациядан жоғары болса, ол қоршаған ортаның қауіпсіздігіне, сондай-ақ тірі организмге теріс әсерін тигізеді және түрлі ауруларға әкеледі. Өртүрлі өндірістік салалардан шығарылған газдағы толуол, ксилол және этилбензол негізгі еріткіштертердің бөлігі болып саналады.

Өндірістік өнеркәсіптерден, мысалы жиһаз, бояу, лак, кабель, полиграфия салаларынан шығарылатын улы газ қалдықтары тірі ағзаларға теріс әсер тигізеді. Осындай органиканың негізгі компоненті – толуол. Мысалы, 2 сағат ішінде 250 мг м^{-3} концентрациясы бар толуолды жұтқанда жүрек жиілігі төмендейді, сөйлеу бұзылып, қозғалыс баяулайды.

Желім, лак, бояудың және т.б. құрамында болатын толуолмен ұзақ дем алатын болса, нейротоксикалық ауытқу клиникалық салдарға, яғни галлюцинация, ұйқышылдық, өз-өзіне қол жұмсау мен көру қабілетінің бұзылуына және құрысуға әкеледі.

Органикалық заттардың толық тотығуы кезінде жоғары белсенділікке ие (95 - 100%) бағалы металдар негізіндегі (Pt, Pd) катализаторлар өнеркәсіптік өндірістерден шығарылған газдарды тазарту үшін қолданылады. Платина тобы металдарының қолжетімділігі мен бағасының жоғары болуы құрамында асыл металдары болмайтын, термотұрақтылығы жоғары, улануға қарсы және ұзақ уақыт аралығында эксплуатациялануға тұрақты, тиімділігі жоғары полиоксидті катализаторларды жасауға деген қажеттілік тудырады. Шығарылған газдарды тазалауға бағалы металдарсыз және құрамында бағалы металдар аз катализаторларды жасау басты мақсат болып саналады.

Өндірістік өнеркәсіптерден шығарылған улы органикалық газдарды толық тотығу технологияларын дамытуда құрамында бағалы металдары жоқ жоғары тиімді полиоксидті катализаторларды жасау да өзекті.

Көлемдік жылдамдығы $5 \cdot 10^3 \text{ с}^{-1}$ мен температурасы 723 К-де толуолдың толық тотығу реакциясында полиоксидті катализаторлардың белсенділігін зерттеу жолдары көрсетілген. Катализаторлар құрамының көбеюі арқылы толуолдың конверсиясы жоғарылады. 5 Ni/2% Ce/ θ -Al₂O₃ катализаторында толуолдың ең төменгі тотығу көрсеткіші 57.0% болса, ал керісінше үш компонентті 9% Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ катализаторда 98.5% ең жоғары тотығу дәрежесі байқалды.

Бастапқы қоспадағы ауа мен толуолдың концентрациясын 100-ден 320 мг^{-3} -ке дейін жоғарылатқанда екі компонентті Ni-Cu/2%Ce/ θ -Al₂O₃ және Cu-Cr/2%Ce/ θ -Al₂O₃ катализаторда толуол конверсиясының дәрежесі төмендейді.

Зерттеу нәтижесі барысында үш компонентті Ni-Cu-Cr/2% Ce/ θ -Al₂O₃ катализаторда оңтайлы Ni : Cu : Cr = 1,0 : 3,0 : 0,1 қатынасында, $5 \cdot 10^3 \text{ сағ}^{-1}$ көлемдік жылдамдықта және 723 - 773 К температурада толудың айналым дәрежесі анағұрлым (98.8%- дейін) жоғарылайды. Оттектің беттік қабатпен байланыс энергиясы және полиоксидті катализатордағы реакциялық қабілеттілігі ТБД, ТБТ және ТБТ әдістері арқылы анықталды. Түзілген Ni және Cu алюминаттары 973-1223 К аралығында Н₂ әсерінен оксидтерге немесе олардың қоспаларына дейін тотықсызданатындығы анықталды.

Ni-Cu-Cr катализаторларында оттегінің адсорбциясы оксидтердің ыдырауынан кейін ең төменгі (325 К) температурада жүреді. Бұл дисперсті оксидтердің адсорбцияланған О₂, О және оттегі торларының жоғары қайта белсенділігін, сондай-ақ олардың қоспаларын оның жеңіл жолмен қайта қосылуға қабілеттілігін көрсетеді.

Түйін сөздер: каталитикалық тотығу, толуол, тазалау, никель, мыс.

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ИССЛЕДОВАНИЕ Ni-СОДЕРЖАЩИХ КАТАЛИЗАТОРОВ ДЛЯ ОЧИСТКИ ОТХОДЯЩИХ ГАЗОВ

Аннотация. Проблема химической безопасности и санитарной защиты воздуха особенно актуальна в связи с увеличением вредных выбросов промышленных предприятий, которые оказывают сильное токсическое воздействие. Многие химические соединения (толуол, ксилол, стирол, фенол, трикрезол, минеральные спирты, СО и т.д.), которые негативно влияют на живые организмы и флору, являются вредными токсичными выбросами от промышленных предприятий. В соответствии с Парижским соглашением, принятым 12 декабря 2015 года и подписанным 22 апреля 2016 года в дополнение к Рамочной конвенции Организации Объединенных Наций об изменении климата, развитые страны и страны с переходной экономикой должны сократить или стабилизировать выбросы парниковых газов. Содержание вредных выбросов выше ПДК в промышленных цехах и атмосферном воздухе в городах оказывает негативное воздействие на живые организмы и приводит к различным заболеваниям, тем самым создает угрозу безопасности окружающей среды. Толуол, ксилол и этилбензол являются основной частью растворителей, используемых в различных отраслях промышленности, которые присутствуют в газообразных выбросах. Токсичное и вредное воздействие вредных выбросов на живые организмы можно проследить на примере толуола - основного компонента токсичных органических газообразных выбросов, которые присутствуют в выбросах мебельной, лакокрасочной, кабельной, полиграфической и других отраслей промышленности. Например, вдыхание толуола с концентрацией 250 мг м^{-3} в течение 2 ч приводит к снижению частоты сердечных сокращений, нарушению речи, координации движений. Длительное вдыхание толуола, который присутствует в составе клея, лаков, красок и т.д., вызывает нейротоксические отклонения, которые приводят к клиническим последствиям - галлюцинациям, сонливости, попыткам самоубийства, нарушениям зрения и судорогам.

Как правило, катализаторы на основе благородных металлов (Pt, Pd), которые обладают высокой активностью (95 - 100%) при полном окислении органических веществ, используются в основном для очистки отходящих газов промышленных предприятий. Условия дефицита и высокая стоимость металлов платиновой группы приводят к необходимости разработки новых подходов к созданию высокоэффективных полиоксидных катализаторов, не содержащих благородных металлов, способных проявлять высокую термостойкость и стойкость к отравлению и устойчивых в течение длительного срока эксплуатации. Создание катализаторов для очистки газов, которые не содержат благородных металлов или содержат их в небольших количествах, является важной целью. В этом контексте актуальны разработки высокоэффективных полиоксидных катализаторов, которые не содержат драгоценных металлов, а также технологии глубокого окисления токсичных органических газообразных выбросов промышленности.

Представлено исследование активности полиоксидных катализаторов в реакции глубокого окисления толуола при 723 К и объемной скорости $5 \text{ ч}10^3 \text{ ч}^{-1}$. Конверсия толуола возрастала с усложнением состава катализаторов. Самая низкая степень окисления толуола 57.0% наблюдалась на катализаторе 5% Ni/2% Ce/ θ - Al_2O_3 , а наибольшая степень 98.5% наблюдалась на трехкомпонентном 9% Ni-Cu-Cr/2% Ce/ θ - Al_2O_3 катализаторе. Увеличение концентрации толуола от 100 до 320 мг м^{-3} в исходной смеси с воздухом приводит к незначительному снижению степени превращения толуола на двухкомпонентных Ni-Cu/2% Ce/ θ - Al_2O_3 и Cu-Cr/2% Ce/ θ - Al_2O_3 катализаторах.

В результате исследований было установлено, что наибольшая степень превращения толуола (до 98.8%) наблюдается на трехкомпонентном катализаторе Ni-Cu-Cr/2% Ce/ θ - Al_2O_3 с оптимальным соотношением Ni : Cu : Cr = 1,0 : 3,0 : 0,1 при объемной скорости $5 \text{ ч}10^3 \text{ ч}^{-1}$ и температуре 723 - 773 К. Энергию связи кислорода с поверхностью и его реакционную способность на полиоксидных катализаторах определяли методами ТПД, ТПО и ТПВ. Было показано, что образующиеся алюминаты Ni и Cu могут восстанавливаться до исходных оксидов или их смесей под воздействием H_2 при 973 - 1223 К. Адсорбция кислорода на катализаторах Ni-Cu-Cr после разложения оксидов происходит при низкой температуре (325 К). Это указывает на высокую реакционную способность адсорбированного O_2^- , O⁻ и кислорода решетки дисперсных оксидов, а также их смесей и его способность к легкой реактивации.

Ключевые слова: каталитическое окисление, толуол, очистка, никель, медь.

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