

Catalytic neutralization of gas emissions in the manufacture of pharmaceutical preparations

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Abstract. Environmental protection in the Republic of Uzbekistan with a developed chemical, petrochemical, metallurgical and pharmaceutical industries is an important problem of our time. To solve it, a domestic copper-chromite catalyst “Chemex-203” was previously developed, which was operated for a long time in an energy-saving reversible reactor RKR-10 in the process of catalytic neutralization of ventilation emissions of highly toxic styrene, toluene and acetone vapors on the territory of the “Hobos-TAPO” joint venture in Tashkent. This paper is devoted to solving a two-sided environmental problem - obtaining copper-chromite catalysts using toxic wastes of local industry for thermal catalytic neutralization of gaseous emissions of volatile organic compounds typical of the pharmaceutical and chemical industries. The conducted studies make it possible to 100% replace imported aluminum hydroxide in the composition of the aluminum-titanium carrier for the copper-chromite catalyst for the complete oxidation of toxic emissions with the intermediate product of the processing of spent alumina adsorbent, including gel-like pseudoboehmite. The resulting catalyst is distinguished by good mechanical strength, chemical and thermal stability and allows highly efficient neutralization of combustible toxic substances in the composition of various gas emissions.

1 Introduction

Pharmaceutical production, along with chemical and oil refineries, as well as household and clinical waste, are currently the main sources of industrial wastewater and air pollution. In the production of pharmaceuticals, organic solvents are widely used, chlorination of intermediate compounds is carried out, during which, as well as incineration of hospital waste, volatile organic compounds with proven carcinogenic properties are released: dichloroethane, aromatic hydrocarbons, vinyl chloride, styrene, and others [1]. The removal of atmospheric pollutants is one of the important areas of international scientific research. Recently, technologies that prevent the emission of chlorinated volatile organic compounds have become especially important due to their stability and ability to form even more toxic secondary substances in the environment [2]. The article by Lykov et al noted that the

progressive growth in the production and consumption of pharmaceutical substances and the associated environmental pollution has already become an international problem that requires due attention [3].

In the production of galenic preparations, the following are widely used as selective extractants of non-polar substances from plant materials: benzene, petroleum and ethyl ether, hexane, chloroform, methylene chloride, ethanol, isopropanol, butanol, acetone and acetic acid. The extraction of salts of alkaloids, furocoumarins, cardiac glycosides, saponins, sugars and vitamins C, K, P and PP is carried out with water-alcohol solutions. The production of synthetic drugs is also accompanied by the release of large amounts of toxic compounds at the stages of chlorination, alkylation, and isolation of target substances. To meet environmental requirements, thermal oxidation systems have been widely used in the disposal of solid waste of pharmaceuticals and concentrated vapors of organic compounds, for example, exhaust gases from the production of monochloroacetic acid, a component in the synthesis of a number of drugs. Combustion is carried out at a temperature of 1200-1700°C to ensure the conversion degree of non-condensed reaction products (vapors of acetic and monochloroacetic acids, chlorine and hydrogen chloride) of at least 95%. The gas stream at the outlet of the thermal oxidation apparatus has a high temperature, which makes it difficult to further clean it from non-combustible chlorine compounds. In the presence of spinel-type catalysts based on oxides of transition metals (Cu, Cr, Co, Ni, Mn), the reactions of deep oxidation of organic compounds with the formation of CO₂ and H₂O proceed at temperatures of 400–600°C; therefore, the thermal catalytic method is effective in the purification of gas emissions from impurities of various solvents, which are often isolated in industrial processes [4-5]. Apparatuses that provide for the recovery of heat [6] released during exothermic reactions have an obvious advantage, since they provide a low temperature of the “tail” gases acceptable for additional purification from acidic impurities by adsorption or absorption methods [7].

2 Experimental technique

In contrast to the “Chemex-203” catalyst, prepared exclusively from imported raw materials, for the synthesis of catalyst carrier No. 1, aluminum hydroxide was used, obtained by dissolving the Shurtan GCIC waste in sulfuric acid, followed by sedimentation of AlOOH with ammonia. The specified waste, the spent alumina adsorbent, contained chemisorbed chelate complexes of Ziegler-Natta polymerization catalysts (VOCl_x, TiCl_x) with deactivators, as well as organometallic catalysts that are easily eliminated into the environment during storage of the specified waste in dumps. The total content of chemisorbed organic substances reached 23-27 wt. %, in terms of carbon from 1.5 to 4.5 wt. from the mass of the spent alumina adsorbent, and the most toxic vanadium from 0.3 to 0.6% of the mass of V₂O₅.

Synthesis of the aluminum-titanium carrier was carried out by mixing AlOOH with 10% crushed spent alumina adsorbent and 25% commercial titanium dioxide, peptized with 10% nitric acid to obtain a plastic mass, molded by extrusion into granules, dried and calcined at a temperature of 500-550°C. When preparing a joint solution of active components for the impregnation of carriers, CrO₃ was first dissolved in water to form H₂CrO₄. Separately, CuSO₄·5H₂O was dissolved in water, Cu₂CO₃(OH)₂ was deposited with NaHCO₃, the resulting residue was washed with water and then gradually introduced into the chromic acid solution. Catalysts No.1 and No.2 were obtained by impregnation of the aluminum-titanium support and calcined granules of the spent adsorbent with a joint solution of Cr and Cu compounds, followed by calcination at a temperature of 550°C, respectively. Acid gases NO_x and CO₂, released during the production of copper chromite

catalysts on industrial equipment, were neutralized in an apparatus with a turbulent gas-liquid layer [7].

The studies were carried out using the following instruments: electron probe microanalyzer JXA 8800R “Super probe” (Jeol), “Dron-3” diffractometer, HESON HS-TGA-103 derivatograph, “Chrom-5” chromatograph with a flame ionization detector, and “Gasochrom 330”. The activity of the catalysts was evaluated by analyzing the products of the oxidation of model substances with atmospheric oxygen, which are formed during their passage through the heated catalyst bed. The volume of the studied catalyst was $\sim 500 \text{ cm}^3$, the layer height was 15 cm. The temperature was varied from 300 to 500°C, and the space velocity of the steam (gas) air mixture was from 10,000 to 50,000 m^3/h .

The depth of oxidative reactions and the degree of conversion of toxic substances to environmentally friendly products in the presence of the synthesized catalysts were judged from the change in the content of the initial compounds and probable products of incomplete oxidation in the gas phase at the outlet of the flow unit. The sensitivity limit of the analysis of initial organic substances and products of incomplete oxidation is $\sim 0.018 \text{ mg/m}^3$, CuO - 0.02 mg/m^3 , CrO₃ - 0.0015 mg/m^3 .

3 Experimental results and their discussion

The spent alumina adsorbent contained chemisorbed chelate complexes of Ziegler-Natta polymerization catalysts (VOCl_x, TiCl_x) with deactivators, as well as organometallic cocatalysts, which are easily eliminated into the environment during storage of the specified waste in dumps. The total content of chemisorbed organic substances reached 23-27% wt., in terms of carbon, from 1.5 to 4.5% of the mass of the spent alumina adsorbent, and the most toxic vanadium, from 0.3 to 0.6% of the V₂O₅ mass.

No organic and organometallic compounds were found in the finished catalyst No.1, and the content of vanadium, in terms of V₂O₅, did not exceed 0.03% wt. The finished catalyst No.2 on the spent alumina adsorbent was distinguished by a lower content of CuO and Cr₂O₃, compared with the “Chemex-203” and No.1 catalysts, the content of vanadium was in the range of 0.2-0.5 % of the V₂O₅ mass, and TiO₂ - 0.06-0.18 %.

The arrangement of thermal effects in the thermograms of dried carriers fully corresponded to the pattern observed when their individual components were heated. In the case of the carrier of catalyst No.1, the endothermic effect from the process of the transition of AlOOH to γ -Al₂O₃ partially overlapped the weak exothermic effects in the region of 270°C from the decomposition of residual NH₄NO₃ ions and 250–550°C from the burnout of organic impurities in the composition of the spent alumina adsorbent additive. Commercial titanium dioxide in the studied temperature range had no thermal effects. In the diffraction pattern of catalyst No.1, reflections from the phases of anatase ($d=3.52; 2.43; 2.38; 2.33; 1.892; 1.699; 1.666, 1.491, 1.480, 1.364, 1.337$ and 1.265 \AA), rutile ($d=3.25; 2.49; 2.19, 1.687; \text{ \AA}$), low-temperature ($d=1.98$ and 1.39 \AA) and high-temperature ($d=2.445, 2.29, 1.988-1.937 \text{ \AA}$) modifications of γ -alumina, as well as Al₂O₃·2H₂O ($d=4.88; 4.39; 2.45; 2.38; 2.05, 1.99$ and 1.92 \AA). The Al₂TiO₅ crystalline phase, a likely product of the interaction between aluminum and titanium compounds, was not detected by X-ray diffraction. In the diffraction patterns of the spent alumina adsorbent and the copper-chromite catalyst based on it, reflections from the α -Al₂O₃ phase ($d = 3.95; 3.48; 2.55; 2.38; 2.29; 2.08; 1.74; 1.61; 1.56; 1.52; 1.40; 1.37$ and 1.24 \AA).

A clear difference between the thermograms of the stripped off impregnating solution, dried samples of catalysts obtained by impregnation of the corresponding carriers and the thermograms of chromium (VI) oxide and basic copper carbonate indicated the formation of new chemical compounds even at the stage of successive dissolution of the initial

components in water. The thermogram of chromium oxide in the studied temperature range is characterized by two endothermic effects: a narrow effect due to the melting of CrO_3 at 196-198°C without weight loss, and a more diffuse one at 210-260°C as a result of its decomposition into Cr_2O_3 and O_2 with a weight loss of 24%. In the thermogram of $\text{Cu}(\text{OH})_2$, CuCO_3 was seen only one intense extended endoeffect at about 220-235°C from its decomposition to CuO with a weight loss of 28%, due to the removal of CO_2 and H_2O . In the low-temperature region of the thermogram of the evaporated impregnating solution, as well as in air-dry impregnated catalytic systems, endothermic effects were observed due to the removal of physically adsorbed (weight loss of about 10% at 75–95°C) and crystallization water (weight loss of 9.55% at 290–350°C) from the hydrated form of copper chromate. The formation of phases of hydrated and anhydrous copper chromate at the intermediate stage of the synthesis of catalysts No.1 and No.2, as well as stripped off impregnating solutions, followed from the appearance of reflections from $\text{CuCrO}_4 \cdot 2\text{CuO} \cdot 2\text{H}_2\text{O}$ with ($d=5.40$; 4.90; 3.62; 3.43; 2.70; 2.57 and 2.4Å) and CuCrO_4 ($d=3.66$; 3.575; 2.712; 2.625; 2.493; 2.231 Å), in the diffraction patterns of samples calcined at a temperature of 300-330°C. The thermal transformation of anhydrous CuCrO_4 with the release of gaseous oxygen manifested itself as a weak endo effect at a temperature of 450°C, was accompanied by weight loss and the formation of CuCr_2O_4 and CuO phases by the reaction $2\text{CuCrO}_4 \rightarrow 2\text{CuCr}_2\text{O}_4 + 2\text{CuO} + 3\text{O}_2$. Endothermic effects due to the formation and thermolysis of copper chromate were clearly manifested in the thermogram of the evaporated impregnating solution, but were barely noticeable in the case of catalysts. According to X-ray phase analysis, after the final calcination of catalysts No.1 and No.2 at 500°C, a mixture of CuO and CuCr_2O_4 crystalline phases was recorded, CuCrO_4 and Cr_2O_3 phases were not detected (Figure 1). According to the results of scanning electron microscopy and chemical elemental analysis, catalyst No.1, like “Chemex-203”, contained from 5.7 to 6.1% wt. CuO and from 9.4 to 10.2 wt % Cr_2O_3 . The amount of active metals chemically bound in copper chromite ranged from 13.9 to 14.5 wt %, and the excess of CuO was in the range of 1-3% wt. The content of TiO_2 was in the range of 21-24%, Al_2O_3 the rest. Copper chromite catalyst No.2, obtained by impregnation of spent alumina adsorbent, was distinguished by a lower content of active components: 4.3% wt. CuO and 6.9 wt % Cr_2O_3 .

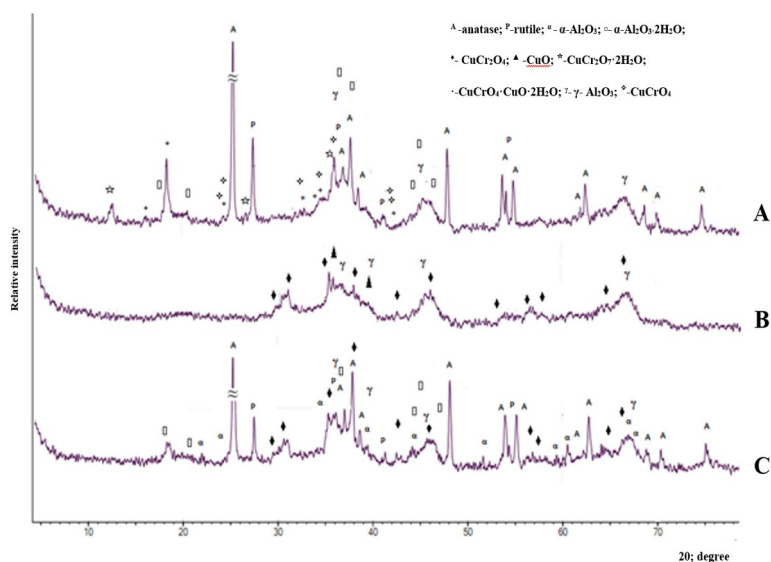


Fig. 1. Diffractograms of the catalysts: A - No.1 calcined at 330°C, B - No.2, calcined at 550°C, C - No.1, calcined at 550°C.

The absence of the Cr_2O_3 phase is a positive factor, since it is known that at high temperatures of the process of deep oxidation of impurities that are difficult to neutralize, especially in gaseous media with a high concentration of aggressive impurities, for example, SO_x , there is a noticeable entrainment of chromium oxide (III) along with exhaust gases. This is especially important in the treatment of gas emissions from pharmaceutical industries using substances such as chlorosulfonic acid, which is used in the production of thiamine, along with methanol. The resistance of catalysts "Chemex 203" and No.1 to the effects of Cl_2 , HCl and HSO_3Cl was proved by the negative results of the gas phase at the outlet of the deep oxidation reactor for the presence of copper and chromium ions. When neutralizing gas-air mixtures $100 \text{ mg/m}^3 \text{ HSO}_3\text{Cl}$ - $600 \text{ mg/m}^3 \text{ CH}_3\text{OH}$; $100 \text{ mg/m}^3 \text{ CH}_2\text{Cl}_2$ - $200 \text{ mg/m}^3 \text{ C}_2\text{H}_5 - \text{O} - \text{C}_2\text{H}_5$ under laboratory conditions, the entrainment of Cu and Cr was not recorded. Previously, ten-day pilot tests were carried out on real gas emissions from the pharmaceutical company FAO "Ferein", where the concentration of identified toxic substances: chloroacetic acid methyl ester, methylene chloride, methanol wavelike changed in a cyclic mode. HCl and Cl_2 were fixed in the reaction products of the first stage of decontamination on the "Chemex 203" catalyst, which were captured at the second adsorption stage using an alumina adsorbent modified with NaOH . No toxic compounds of copper and chromium were found in the exhaust gases of both the first and second stages.

The most important criterion for the selection of catalysts intended for the neutralization of carbon-containing compounds in gas emissions is the depth of interaction of toxic impurities with atmospheric oxygen. Comparative tests carried out on a pilot plant revealed that under identical experimental conditions, 99 percent oxidation of individual test substances: acetone, xylene and styrene to CO_2 and water on catalysts "Chemex-203" and its analogue catalyst No.1 is achieved at the same temperature. Whereas on catalyst No.2, an acceptable degree of conversion is achieved at a temperature 5-15°C higher. At lower temperatures, the reaction products were dominated by products of incomplete oxidation, primarily toxic CO . In separate experiments it was shown that at an initial CO concentration of 1000 mg/m^3 and a low volumetric velocity of the purified air – 10000 h^{-1} , 99 % of CO is converted into CO_2 at 310°C. A doubling of the space velocity is accompanied by an increase in the temperature of reaching this milestone up to 350°C, and with a fivefold acceleration, the deep oxidation process must be carried out at a temperature not lower than 380°C. 99.9% CO conversion is achieved at 400°C.

Using the example of neutralization of acetone vapors, it is shown that at 290°C 77-85% of acetone is oxidized to CO_2 , 13-17 % is converted into acetic acid, about 1-2% into formic acid. At a temperature of 425-450°C and 99.9 % conversion (the sensitivity limit of the analysis method), organic compounds and CO are no longer detected. Phthalic anhydride was found among a number of unidentified products of incomplete oxidation on all the studied catalysts during the oxidation of xylene vapor, as well as styrene, in the temperature range of 300-400°C. On catalyst No.2, the degree of xylene conversion at 425°C did not exceed 88.5%, and at 380°C it was only 40.5% at a very low degree of oxidation. In addition to the temperature factor, we associate the increased formation of phthalic anhydride with a lower concentration of active components in catalyst No.2, as well as with the known ability of vanadium compounds to stimulate predominantly reactions of mild oxidation of organic substances. It should be noted that the monitoring of the operational efficiency of the RKR-10 industrial reactor, where the "Chemex 203" catalyst bed reached 50 cm, the air supply and the process temperature of 400-450°C were optimized, the degree of oxidation of harmful impurities was in the range of 98.8 -99.9 %.

When the vapor concentration fluctuated from zero to 1800 mg/m³ of styrene, up to 300 mg/m³ of acetone and up to 1200 mg/m³ of toluene, the CO₂ concentration in the treated gas emissions varied from 10 to 10000 mg/m³. At the same time, carbon monoxide and phthalic anhydride were not found in the composition of the oxidation products. Taking into account the inevitable formation of large amounts of CO₂ during the catalytic complete oxidation of toxic substances, as well as the presence of non-combustible acidic impurities in the composition of many emissions, we tested a technological scheme for capturing and irreversibly binding HCl, SO₃ and CO₂ in an apparatus with a turbulent gas-liquid layer in the pilot production of UzCPRI [7-8], where solutions of sodium and calcium hydroxides were used as the liquid. To capture CO₂ from exhaust gases, we also tested a variant of adsorption post-treatment on the zeolite of type A and X developed by us, which can be used at low gas flow rates.

Chemical analysis of the gas phase also showed the absence of vanadium, chromium and copper compounds among the gaseous products of oxidation of a multicomponent mixture of combustible substances. That is, the fact of encapsulation of a volatile toxic impurity of vanadium and supported transition metals during the preparation of all studied copper-chromite catalysts using vanadium-containing spent alumina adsorbent has been ascertained. The encapsulation of environmentally harmful impurities prevents the possibility of secondary pollution of the atmosphere by heavy metal compounds in the process of neutralizing gas emissions.

The performance of continuous catalytic oxidation of toxic organic substances is much higher than that of adsorption treatment. But its implementation is associated with significant energy costs, since the reactions of deep oxidation of hydrocarbons proceed at high temperatures. Therefore, in case of periodic formation of low concentrated emissions (10-0.2 mg/m³) of substances with a low MPC value, it is rational to combine adsorption and catalytic methods in one device. For example, styrene, used to obtain various plastic masses, is one of the most toxic hydrocarbons. Its maximum permissible concentration in the air of populated areas is 0.003 mg/m³, i.e. 3 times less than the MPC of such a toxic substance as hydrocyanic acid. Taking into account the specifics of the formation of gas emissions at a number of industrial enterprises, we have shown the fundamental possibility of using the "Chemex-203" catalyst and its analogue catalyst No.1 in the adsorption-catalytic mode for the neutralization of low-concentration vapor-air mixtures of derivatives of aromatic hydrocarbons, aldehydes and ketones, similarly to the purification of air from styrene carried out by manganese-containing catalysts, which also include precious metals [8].

When implementing this approach, first, purification is carried out due to the chemisorption interaction of organic molecules with the catalyst surface under conditions of pre-catalysis at low temperature. The duration of the adsorption stage depends on the content of impurities in the purified gas and the adsorption capacity of the catalyst. Periodic release of the surface occurs at the next stage, where due to the deep oxidation of chemisorbed impurities at a high temperature, which ensures the conversion into harmless gaseous reaction products, the catalyst is regenerated. A necessary condition for the implementation of adsorption-catalytic processes is the irreversible sorption of impurities on a given catalyst at sufficiently low temperatures. We found that the surface of catalyst No.1, as well as "Chemex 203", has a good sorption capacity with respect to derivatives of aromatic hydrocarbons and acetone, carbon monoxide is retained somewhat worse at temperatures of 20-50°C. This is evidenced by the absence in the gas at the outlet of the catalytic reactor of both initial organic substances, as well as CO and any products of complete or partial conversion in the initial section of the dependence curves of the conversion degree on the temperature of the oxidation process, both individual substances and their model mixtures. (Figure 2).

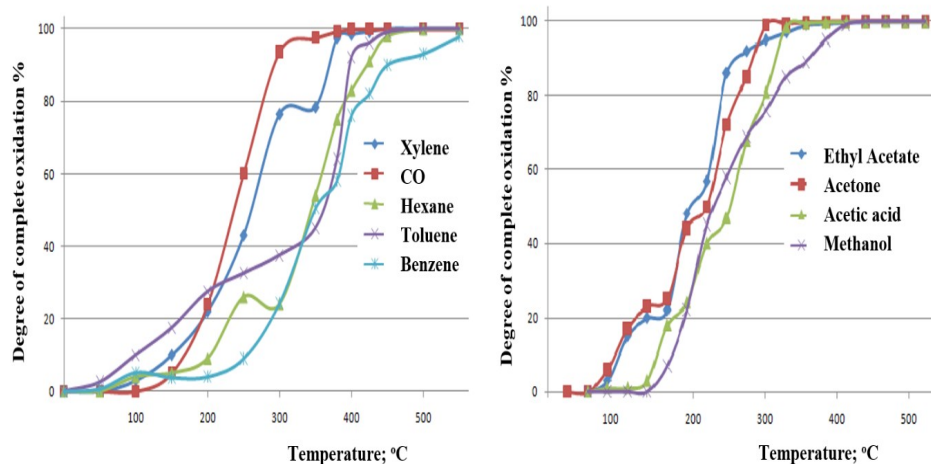


Fig. 2. Dependence of deep oxidation degree of substances model mixtures typical for gas emissions in the production of pharmaceuticals.

Comparison of the dependence degree of deep oxidation of model mixtures on temperature, shown in Figure 2 with the results of experiments on the transformation of the same individual substances, revealed the presence of the effect of "reactive adsorption and catalytic oxidation" [5], when the temperature of the complete transformation of the starting substances in mixtures by 10-15°C exceeded the transformation temperature of individual substances.

4 Conclusion

Thus, the conducted studies have revealed the possibility of 100% replacement of imported aluminum hydroxide in the composition of the aluminum-titanium carrier for the copper-chromite catalyst for the complete oxidation of toxic emissions by the intermediate product of the processing of spent alumina adsorbent, including gel-like pseudoboehmite $AlOOH$. The resulting catalyst is characterized by good mechanical strength, chemical and thermal stability and allows highly efficient neutralization of combustible toxic substances in the composition of various gas emissions in the production of pharmaceuticals and related areas of the chemical industry.

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