Catalytic Carbon-Containing Composition for Phosphine Oxidation

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Abstract. Sorbent for removal of phosphine from furnace gas based on special coke from the Shubarkol field was investigated. The composition coke + CuO (10 wt.%) + ZnO (0.1 wt.%) + Cr₂O₃ (1 wt.%) showed a high sorption capacity for PH₃ - about 130 mg / g for 24 h.

1. Introduction
Gas purification in the chemical industry is a complex and urgent problem that has a number of aspects.

Transition of chemical production to new gas cleaning methods and systems is highly encouraged. However, such a task bears several technological difficulties. New methods could be based on: the latest achievements of science and technology around the world; the modernization of ineffective gas separation plants; the creation of highly efficient equipment and schemes for removing gaseous and aerosol impurities from gas streams; unification and standardization of gas cleaning equipment are required, etc.

The economic aspect of the development of such new methods and systems is a significant increase in the recovery of valuable components and raw materials. A maximum utilization of products captured during gas cleaning and increasing the efficiency of equipment operation also bears certain profit.

Environmental aspects include reducing the specific emissions of pollutants into the atmosphere to sanitary standards; elimination of salvo emissions of harmful substances associated with equipment maintenance and accidents; creation of closed gas-air systems and waste-free technologies, etc. [1].

A significant amount of furnace gas (4 t/t of product) is generated at enterprises during electrothermal production of yellow phosphorus and its derivatives. This is due to the relatively low quality of phosphate raw materials and the imperfection of the existing processing technology. For example, 4969.36 t/year of gaseous substances are emitted into the atmosphere during the production of 110000 tons of yellow phosphorus only in the Zhambyl branch of Kazphosphate - NDFZ LLP. The specific yield of furnace gas at phosphorus enterprises is 2800-3000 m³ per 1 ton of phosphorus [2].
Furnace gas formed during phosphorus production contains mainly CO (85-95 vol.%). It is accompanied with impurities PH₃, P₂O₅ and gases H₂S, HF (0.1-2.0 vol.%). The most harmful components of the furnace gas are PH₃, P₂O₅. Due to the presence of toxic substances, the furnace gas cannot be used either for the synthesis of valuable organic products, or as a process fuel. Most often, gas is burned on the flare stack, which leads to an intense environmental pollution [3].

About 3-6 GJ of thermal energy is irretrievably lost as a result of waste gases combustion on flare stacks. As a result, up to 3×10⁸ m³ of furnace gas is consumed, which could replace up to 1×10⁸ m³ of natural gas. Thus, furnace gas of phosphorus production needs to be purified because it is a constant source of pollution both from a technological and environmental point of view. Compounds of phosphorus, fluorine, sulfur pollute the soil, surface runoff and are partially filtered into the aquifers. There is a threat of pollution of underground waters for drinking purposes and the danger of accumulation of toxic compounds in agricultural products [4-6].

Sorption and catalytic methods for removing pollutants are the main ways to improve the system for cleaning gas and dust emissions. Both the catalytic reactor for oxidizing phosphorus containing gases [7-9] and the catalyst itself can be upgraded.

The catalyst for removing PH₃ from the gaseous medium can be in the liquid phase. For example, it can be a mixture based on H₂O₂ [10], an expensive ionic liquid with Pd [11, 12], a multicomponent solution containing Ag⁺ salts [10, 13]. The electrochemical approach using a Ti/ SnO₂ anode is possible [14].

Passing contaminated gas through a bed of catalyst-sorbent is the most common method for purifying gas mixtures, including furnace gases, from phospheine production. Various types of carbon are often used as a substrate for the catalyst: coke [15], Carbon Nanotubes [16], Activated Carbon [17-19], activated walnut-shell carbon [20,21] peach and apricot carbon [13], carbon fiber in the form of a sorption-active tissue [21]. Also, halloysite-nanotubes [22, 23], modified diatomite absorbent [24], TiO₂ [25, 26], 13X zeolite [27, 28] can be used.

Fe₂O₃, Co₃O₄, NiO,CoP, NiP₂, FeP[16], nano-sized amorphous alloys particles CoB, CoP, CoBP [26], nanoparticles FeNi and BFeNi [22], Ni+NiFe₂O₄ [23], Cu-Fe nanocomposites [24], Ni/Fe₂O₄ [25], Zn/Fe+Cu [29], ZnO+La₂O₃ [18], Cu-Fe-Ce (La) [30] can be used as active impregnated components.

The catalyst for PH₃ removal contains Cu compounds [15, 27, 31, 32]. Additional chemical activation of activated carbon can be carried out by treatment with KOH [19, 20] and HCl [17].

The catalytic removal of PH₃ from flue gas is a complex multistage process. Authors of [33] showed that 74 reactions can occur simultaneously when using CuO as an adsorbent, taking into account the effect of different contents of N₂, CO, O₂, H₂ and when changing the temperature in the range 0-100 °C. The oxidation process of PH₃ is greatly influenced by the temperature and the number of water clusters in to the system [34].

Earlier [15], a high activity of the catalytic composition of the composition coke + 8-10 wt.% CuO + 0.3-0.6 wt.% ZnO + 0.8-1.3 wt.% Cr₂O₃ for 160 min was shown in the process of cleaning the furnace gas of LLP "Kazphosphate" NDFZ from PH₃, P₂O₅, H₂S, etc. In this work, the catalytic properties of a similar composition, characterized by a reduced content of ZnO (0.1 wt.%), were studied for a longer time - 24 h.

2. Experimental

2.1. Materials
Granular special coke on the basis of coal "D" of the Shubarkol field was used as the carbon carrier. Sequential activation was carried out with sharp water vapor and then with a mixture of gases to develop the adsorption surface of the carbon carrier.

Carbon catalysts were prepared by impregnation by solutions of Zn(CH₃COO)₂, (NH₄)₃[Cr(C₂O₄)₃], (NH₄)₃[Cu(C₂O₄)₂] salts, similar to [16]. The resulting carbon-catalytic
composition was calcined in a muffle furnace in an air atmosphere until the salts were completely decomposed to oxides.

2.2. Methods
The concentration of oxides in the solid residue was determined by atomic absorption spectroscopy on the spectrometer AANALYST 400 cHGA 900 Perkin Elmer», 2012г.

The thermolysis of impregnated coke was carried out using the equipment STA 409 PC Luxx (NETZSCH, Germany, 2009) in a dynamic air atmosphere (argon protective gas flow rate – 20 ml·min⁻¹) at heating rates of 10°C·min⁻¹ in the temperature range of 30–1000 °C. 10 mg of the sample was placed in Al₂O₃-crucible.

Phosphine adsorption was studied using the apparatus shown in Figure 1 [36, 37]. The study was carried out at room temperature. The gas mixture in a balloon (1) was fed into a reactor (4) with a diameter of 10 mm, into which 5 g of catalyst (5) was placed. The gas flow rate (0.35 L / min) was measured with a rheometer (3) and regulated with a gas reducer (2). At the outlet of the reactor, the gas mixture entered the “Kometa M5” gas analyzer (6) to determine the PH₃ concentration. The range of measured concentrations is 0.1-2.0 mg/m³. The detection limit is 0.1 mg/m³. Data was recorded every 9-10 seconds.

![Figure 1](image_url)

**Figure 1.** Schematic of a apparatus for studying the sorption of phosphine from a gas mixture. 1 - Cylinder with a mixture of gases (Ar - 99.9%, PH₃ - 0.01%); 2 - Reducer; 3 - Rheometer; 4 - Reactor; 5 - Adsorbent; 6 - Gas analyzer "Kometa M5"

2.3. Methodology of sorption purification of furnace gas
The tests were carried out similarly to [16]. Test parameters for catalytic cleaning of furnace gas: furnace gas flow 500 dm³/min, load weight of carbon-catalytic system - 43 kg, volume of metal dregel with coke + metal oxides catalytic system 0.03 m³, gas sampling temperature - 29-32 °C, sampling and samples were analyzed every 30 minutes for 24 hours.

3. Results and discussion
Tests for deep cleaning of furnace gases using carbon-catalytic systems impregnated with oxides of active metals were carried out in furnace shop No. 5 of Kazphosphate LLP. The composition of the furnace gas is presented in Table 1. The averaged results of the furnace gas cleaning tests are presented in Table 2.
Table 1. The average composition of the furnace gas of LLP "NDFZ-Kazphosphate" (furnace No. 5 SUPG).

|       | P₄, mg/m³ | P₂O₅, mg/m³ | PH₃, mg/m³ | F, mg/m³ | S₂, mg/m³ | CO₂, mg/m³ | PH₃, % (vol.) | CO, % (vol.) | O₂, % (vol.) | H₂, % (vol.) | CH₄, % (vol.) |
|-------|------------|--------------|------------|----------|-----------|------------|--------------|--------------|--------------|--------------|--------------|
| 174   | 183        | 750          | 5.0        | 415      | 0.7       | 0.2        | 67.3         | 2.1          | 1.4          | 0.5          |

Table 2. Phosphine oxidation test results

| Test duration | Defined components | MPC (mg/m³) | Before cleaning, (mg/m³) | After cleaning, (mg/m³) | The purification efficiency, (%) |
|---------------|--------------------|-------------|-------------------------|-------------------------|---------------------------------|
| 0-12 h        | P₄                 | 0.1         | 372.832                 | traces                  | 100                             |
|               | P₂O₅               | 1           | 905.372                 | traces                  | 100                             |
|               | PH₃                | 0.1         | 1588.213                | 2.843                   | 99.5                            |
|               | H₂S                | 10          | 492.223                 | 380.719                 | 22.7                            |
|               | SO₂                | 10          | 937.861                 | 539.642                 | 42.5                            |
|               | HF                 | 0.1         | 1.213                   | traces                  | 100                             |
|               | P₄                 | 0.1         | 280.872                 | traces                  | 100                             |
|               | P₂O₅               | 1           | 734.284                 | traces                  | 100                             |
|               | PH₃                | 0.1         | 1206.592                | 9.295                   | 99.3                            |
|               | H₂S                | 10          | 503.351                 | 402.783                 | 20.0                            |
|               | SO₂                | 10          | 974.183                 | 872.367                 | 10.5                            |
|               | HF                 | 0.1         | traces                  | traces                  | 100                             |

For comparison, we show the values of the average tolerable daily intake for the air in the working area according to GOST [35]. The obtained catalytic composition coke + transition metal oxides exhibits a high catalytic activity throughout the entire purification period in relation to PH₃, P₄ and P₂O₅. The cleaning activity begins to decrease after 24 hours of operation. This can be explained by deactivation of the catalyst with SO₂.

Thus, we conclude that a preliminary cleaning of furnace gases from sulfur-containing contaminants must be carried out in order to increase the number of catalyst cycles.

STA analysis was performed to study the temperature range in which the investigated catalytic system can be used. The thermogram of the obtained catalytic composition is shown on Fig. 2.
The system coke + transition metal oxides does not undergo significant changes when heated to ~ 100° C. A sharp weight loss, which is accompanied by a strong exothermic effect, is not observed even when the system is heated to 1000 °C in air despite the fact that the raw material is coke, a carbon carrier. Therefore, no ignition occurs. This lowers the safety requirements for the storage of the catalytic composition.

4. Conclusions
The composition coke + CuO (10 wt.%) + ZnO (0.1 wt.%) + Cr2O3 (1 wt.%) showed a high sorption capacity for PH3 - about 130 mg/g during 24 h. The obtained carbon catalyst is a promising material and can be used for a deep purification of furnace gases of the phosphorus industry, for example, at LLP “NDFZ-Kazphosphate”. This catalyst composition will be supplemented with sulfur-retaining components in the course of the further work.

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