Technology Of Modified Sodium-Aluminum Catalysts For Nitrogen Gas Purification Systems

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ABSTRACT

The introduction of the method of chemical trapping of nitrogen oxides in a complex with selective catalytic purification of tail gases from industrial production makes it possible to increase the service life of the catalyst regardless of the NOx concentration, create a cycle of low-waste technology and achieve significant savings in the consumption of the scarce AVK-10 catalyst ... Reuse of the spent catalyst AVK-10 in the process of cleaning tail gases of industrial production from NOx and absorption-catalytic cleaning of the latter with the use of solid waste products allows simultaneously solving environmental and economic problems in the production of weak nitric acid.

The prospect of using the waste of lead-concentrating factories as a natural sorbent-catalyst in gemological is substantiated. processes of purification of waste gases of sulfuric acid production.

The proposed chemisorption-catalytic method for purifying waste gas mixtures from sulfur dioxide does not require special preparation of a wet, high-temperature dusty gas. The use of natural materials within the framework of this method allows you to extract from them valuable raw materials - metal oxides.

KEYWORDS

Gas, chemically, mechanism, purification, removals, operating mode, oxide, sorbent
INTRODUCTION

The results of our studies have shown that the comparatively low activity and productivity of aluminum-vanadium catalysts are due to a limited approach to the study of this catalytic system. When setting up this work, extensive studies of the Al2O3-V2O5 system were carried out by modifying them with oxides Fe2O3, Cr2O3, NiO, CaO, as well as alkaline and alkaline-earth elements, and the results of changing the preparation technology and heat treatment conditions were studied [1].

The influence of the nature and concentration of modifiers of iron oxide and manganese dioxide on the properties of the initial and spent catalyst AVK-10, intended for the purification of gas emissions from NOx, has been investigated. The ranges of the investigated mass fractions for iron oxide and manganese dioxide were 0.06 to 7.0; the latter were introduced both separately and in various combinations [2]. The choice of added additions was made based on the analysis of scientific and technical literature and the properties of the oxides of the corresponding additives.

MATERIAL AND METHODS

To establish the modifying effect of the added additives separately and in their various combinations, complex studies were carried out using the methods: electron paramagnetic resonance (EPR), IR spectroscopy, EDS, and the temperature-programmed reduction curve (CTPR). The study of the activity of the synthesized catalysts was carried out in laboratory, experimental and industrial installations for the purification of tail gas from NOx. A series of alumovanadium catalysts prepared by various methods and containing 10% V2O5, 0.1-10% wt. Was synthesized and studied. Fe2O3 and (or) 0.1 to 10 wt%. Cr2O3, and (or) 1% NiO, CaO, as well as oxides of alkali and alkaline earth metals [3]. To obtain the catalysts, the corresponding salts of the active components were mixed with alumina hydrate, impregnated with a molded γ-Al2O3 solution of ammonium metavanadate and nitric acid salts of modifying additives, as well as an industrial alumovanadium catalyst AVK-10 with solutions of modifier salts. After drying (in the case of a mixed-type catalyst) and drying, the catalysts were subjected to heat treatment at 580 °C for 6-8 h.
Table 1 shows the compositions of the compositions applied to the AVK-10 catalyst.

| No. of samples | Fe2O₃% mass | Cr₂O₃ | NiO | CoO | Li₂O, Na₂O, K₂, Rb₂O, Cs₂O | ZnO, CaO, BeO, MgO | B₂O₃ |
|----------------|-------------|-------|-----|-----|---------------------------|-------------------|------|
| 1-7            | -           | 0,1-10| -   | -   | -                         | -                 | -    |
| 8-14           | 0,1-10      | -     | -   | -   | -                         | -                 | -    |
| 15             | -           | -     | 1,0 | -   | -                         | -                 | -    |
| 16             | -           | -     | -   | 1,0 | 1,0                       | -                 | -    |
| 17-21          | -           | -     | -   | -   | -                         | 1,0               | -    |
| 21-24          | -           | -     | -   | -   | -                         | -                 | 1,0  |
| 25             | -           | -     | -   | -   | -                         | -                 | -    |
| 26             | 4,0         | 1,0   | -   | -   | -                         | -                 | -    |
| 27             | 4,0         | -     | 1,0 | -   | -                         | -                 | -    |
| 28             | 4,0         | -     | -   | 1,0 | -                         | -                 | -    |
| 29             | 4,0         | -     | -   | -   | -                         | -                 | -    |

Preliminary tests of synthesized samples based on AVK-10 showed that, in terms of the degree of purification of model gas mixtures from NOx at a temperature of 240-350 °C, catalysts with additions of Fe₂O₃, Cr₂O₃, NiO and CaO are superior to samples containing alkaline and alkaline earth elements. The latter exhibit a promoting effect only at the beginning of the experiment, and then a decrease in the activity of the initial AVK-10 catalyst is observed [4].

In this regard, further studies of catalyst samples containing alkaline, alkaline earth oxides, and boron oxide were discontinued.

The introduction of oxides of iron, chromium, nickel and cobalt into the composition of the AVK-10 catalyst, both individually and in combinations, does not significantly affect its physicochemical and structural-mechanical properties. In this case, the mechanical strength of the catalysts increases from 40 to 45 kg/cm²,
the bulk density from 0.55 to 0.7 kg/l, the total porosity slightly decreases, although the specific surface area of the samples increases from 180 to 195 m²/g. According to the literature data, an increase in the specific surface area can be explained by the appearance of a secondary microporous structure upon the introduction of modified additives [5]. Similar changes in the physicochemical and structural and mechanical properties are observed in modified catalysts prepared on the basis of the γ-Al₂O₃ support, obtained from aluminum hydroxide of the Dneprodzerzhinsk Petrochemical Complex. Modified catalysts based on this support are characterized by higher mechanical strength (65-78 kg/cm²), bulk density (0.7-0.84 kg/l) and porosity (64-80%) as compared to catalysts based on AVK-10. These changes are mainly related to the substrate. Differences in carriers may be due to the structural properties of the initial aluminum oxide hydrate, the presence of impurities, rheological properties and moisture of the formed pastes. Consequently, the prehistory of carriers of the same composition plays an important role in the synthesis of vanadium catalysts for the reduction of nitrogen oxides [6].

Some hardening effect of modifiers is explained by the filling of the contact points between the carrier particles during heat treatment.

To prepare mixed-type alumovanadium catalysts, the calculated amount of A₁(OH)₃ with an absorption coefficient of 35% was loaded into a mixer and NH₄VO₃ dissolved in water with the addition of oxalic acid was added thereto. To modify the catalyst, the calculated amount of nitric acid salts of Cr, Fe, Ni, and Co was dissolved separately. The mixture was thoroughly mixed until a homogeneous mass was obtained [7]. Paste with pp. 28-32% were molded on a 5x5 mm screw press. After drying for 12-16 h, the granules were dried at 110-120 °C and calcined at 580-600 °C for 6-8 h.

When Fe₂O₃, Cr₂O₃, NiO and CaO are added to the Al₂O₃-V₂O₅ system, its mechanical strength increases from 87 to 100 kg/cm². At the same time, the bulk density of the contacts increases, and their porosity and specific surface area decrease. An increase in strength with the introduction of nitric acid salts of modifying additives is due to peptization of aluminum oxide hydrate and the formation of a partial nitrate boehmite under the action of a weak solution of nitric acid released during dissolution of nitric acid salts of the corresponding modifiers. The decrease in porosity and specific surface area is explained by the sintering of small pores during the calcination of amorphous pseudoboehmite particles under the action of iron, chromium, nickel and cobalt oxides [8].

RESULTS

To optimize the component composition of the modified alumovanadium catalyst, samples of the following composition (wt. ppm) were synthesized:
ABK-10 Fe₂O₃-0.06 7.0
ABK-10 MnO₂-0.06
ABK-10 Fe₂O₃-5.0+MnO₂-0.06 7.0
ABK-10 0.06 5.0+ MnO₂-4
The catalysts were prepared by impregnating an AVK-10 sample (substrate), previously dried at 473 °K, with aqueous solutions of iron and manganese nitrate salts or their mixture. The concentration of these solutions corresponded to 350 kg/m³. Depending on the content of the added additives, the impregnation was carried out once or twice. Then the catalysts were dried at 473 °K and, to convert the salts into the corresponding oxides, they were subjected to final heat treatment at 853 °K. With the introduction of Fe₂O₃ and MnO₂, a symbatic increase in the mechanical strength of the AVK-10 catalyst is observed, and the strength increases with an increase in the concentration of the added additives. The specific surface area of the catalyst also increases from 1.8 * 10⁵ to 2.0 * 10⁵ m²/kg. With the combined introduction of Fe₂O₃ + MnO₂, the formation of catalysts is accompanied by a relatively large increase in mechanical strength, but a decrease in porosity.

Table 2

Comparative Activity of Modified Al₂O₃-V₂O₅ Catalysts Prepared by Various Methods

| The composition of the introduced modifiers, wt% | NOx content, % vol. | Power CLEANING, % |
|-----------------------------------------------|---------------------|-------------------|
|                                               | before cleaning     | after cleaning    |                  |
| Fe₂O₃, Cr₂O₃, NiO, CoO                        |                     |                   |
| AVK-10 based catalysts                        |                     |                   |
| 5,0                                           |                     |                   |
| 4,0                                           |                     |                   |
| 4,0                                           |                     |                   |
| 4,0                                           |                     |                   |
| Exodus. AVK-10                                |                     |                   |
| 90%                                           |                     |                   |
| 5,0                                           |                     |                   |
| V₂O₅ modifiers for γ-Al₂O₃                    |                     |                   |
| 90%                                           |                     |                   |
| 5,0                                           |                     |                   |
| -                                              |                     |                   |
| -                                              |                     |                   |
Mixed Vanadium Catalysts

| 5,0 | - | - | - | 0,40 | 0,134 | 66,4 |
| 5,0 | - | - | - | 0,38 | 0,050 | 86,9 |
| - | 1,0 | - | - | 0,42 | 0,119 | 71,6 |
| - | - | 1,0 | - | 0,39 | 0,120 | 69,3 |
| - | - | - | 1,0 | 0,40 | 0,129 | 70,1 |

Therefore, their promoting role is minimized, although there is an increase in activity by 4-20% compared to the original alumovanadium catalyst [9].

Modified catalysts prepared on the basis of γ-Al₂O₃ from pseudoboehmite occupy an intermediate position in activity:

AVK-10 > V₂O₅ on γ-Al₂O₃ > V₂O₅ on γ-Al₂O₃ (mixed). The results show that iron oxide is characterized by the highest promoting efficiency. Modification of the catalyst with iron oxide in combination with other oxides does not give a sufficient synergistic effect. Thus, when the sample contains 4% Fe₂O₃, the activity of the AVK-10 catalyst increases by 10%, with 5% Fe₂O₃ - by 20%, while the introduction gives:
Figure: Activity of spent catalysts AVK-10 depending on the volume fraction of NOx in the gas mixture.

\[
\begin{align*}
4\%Fe_2O_3+1\%Cr_2O_3, 4\%Fe_2O_3+1\%NiO & \text{ and } 4\%Fe_2O_3+1\%Cr_2O_3 > \\
\text{ABK-10}+4\%Fe_2O_3+1\%CoO & \text{ ABK-10}+4\%Fe_2O_3+1\%NiO > \\
\text{ABK-10}+1\%Cr_2O_3 & \text{ ABK-10}+1\%CoO \text{ ABK-10}+1\%NiO. \\
\end{align*}
\]

To increase the service life and efficiency of the catalyst, the following were studied: activity, conditions for the formation and change in the structure of surface centers with vanadium, iron and manganese ions [9].

Comparative studies of the activity of synthesized catalyst samples and commercial AVK-10 were carried out at temperatures of 523 573 °K, gas space velocity of 10000 m3/h, NOx: NH3 = 1: 1.2 (mol) ratio.

The volume fraction of NOx in the tail gas varied within the range: from 0.18 to 0.61. The duration of each experiment was 20 hours. Table 3 shows the activity of the samples of the catalyst AVK - 10, modified with Fe2O3 - 0.05 7.0 (mass parts).

From the table below it can be seen that with an increase in the content of iron oxides in the composition of AVK-10, the activity of the catalyst increases, reaching a maximum at 5.0 (wt. H.). With an increase in the temperature of the process, the degree of purification increases only for samples with a Fe2O3 content of 0.06-5.0 (mass, h), and in all other cases it decreases, which can be explained by a general decrease in selectivity with

Table. 3

Comparative activity of the AVK-10 catalyst modified with Fe2O3 (NOx: NH3 = 1: 1.2 (mol)), the volume fraction of NOx in the feed gas is 0.5.

| Temperature process 0K | The degree of gas purification from NOx (%) on the AVK-10 catalyst, modified with Fe2O3, (mass, h) | AVK-10 industrial design |
|------------------------|-------------------------------------------------|--------------------------|
|                        | 0,06  | 0,10 | 1,0  | 4,0  | 5,0  | 7,0  |                      |
| 513                    | 86,5  | 94,1 | 94,4 | 97,2 | 99,01| 96,5 | 75,6                  |
| 533                    | 85,9  | 94,2 | 94,7 | 97,6 | 98,50| 96,7 | 76,4                  |
| 553                    | 85,7  | 94,8 | 95,1 | 97,1 | 98,30| 96,4 | 77,8                  |
an increase in the content of Fe₂O₃. The decrease in the activity of the catalyst containing Fe₂O₃ - 7.0 (mass, h.), As shown by studies by EPR and KTPR, is associated with an increase in the proportion of structures with a bond - Fe - O - V by the appearance of bulk oxide formations with bonds - Fe - O - Fe formation of a free Fe₂O₃ phase, as well as a decrease in the reduction temperature. It is known that iron ions have a high oxidizing ability. Paired with vanadium (Fe³⁺ and V³⁺+V⁴⁺), these properties change and have a positive effect on the activity of the catalyst at Fe₂O₃ - 0.06-1.0 (mass, h.), in which the bond - V - O - Fe -. The deterioration in the selectivity of the catalyst with an increase in the Fe₂O₃ content is explained by the partial realization of a bulk neoplasm with the - Fe - O - Fe - bond and the Fe₂O₃ phase. which at high temperatures acts as a catalyst for the oxidation of ammonia [10]. Approximately the same pattern of changes in activity is observed with the introduction of MnO₂ into the composition of AVK-10 - 0.06-7.0 (pbw). Here, also, with an increase in the composition of the catalyst MnO₂ from 0.06 to 4.0 (wt, h.), The activity of the catalyst increases, with a further increase to 5.0 (wt. H.), It almost does not change, and at 7,0 (mass, h), the rate of NOx reduction with ammonia begins to decrease.

DISCUSSIONS

1. A technology has been developed for the utilization of waste industrial alumovanadium catalyst AVK-10 to obtain a modified catalyst AVJK-10 for systems for cleaning tail gases from NOx, based on heat treatment of production wastes with subsequent modification with iron and manganese oxides [11].

2. Using the methods of electron paramagnetic resonance (EPR) and the curve of thermoprogrammed reduction (KTPR), the mechanism of the modifying action of the additives introduced into the composition of the alumovanadium catalyst AVK-10 separately and in their various combinations was established.

3. The activity and physicochemical properties of modified alumovanadium catalysts have been studied.

4. The properties of the spent industrial catalyst AVK-10 have been investigated. A decrease in the proportion of large catalyst granules from year to year was noted. It is shown that the structural changes in the catalyst are associated mainly with the reduction of V⁵⁺ + and V⁴⁺ ions to the lowest oxidation state.

5. The synthesis was carried out and the study of the properties and characteristics of modified catalysts based on the spent catalyst AVK-10 was carried out.

6. Using a complex of physicochemical research methods, the catalytic systems A₁₂O₃-V₂O₅, A₁₂O₃V₂O₅-Fe₂O₃, A₁₂O₃-V₂O₅-MnO₂, Al₂O₃-V₂O₅-Fe₂O₃-MnO₂ have been studied. The factors responsible for the high activity of the catalyst have been determined [12].

CONCLUSIONS

The prospect of using the waste of lead-concentrating factories as a natural sorbent-catalyst in gemological is substantiated. The proposed chemisorption-catalytic method for purifying waste gas mixtures from sulfur dioxide does not require special preparation of a wet, high-temperature dusty gas. The use of natural materials within the framework of this method allows you to extract from them valuable raw materials - metal oxides[13].

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