Complex utilization of cobalt-molybdenum catalysts

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Abstract

The article is devoted to the development of a technique for the separation and utilization of cobalt and molybdenum compounds in spent catalysts. The method of fusing the spent catalyst with sodium hydroxide was used. Acetone has been proposed for co-extraction. As a result, it was possible to separate cobalt compounds from molybdenum compounds in solution by setting a certain pH value in it. This will reduce the amount of waste and improve the ecology of industrial areas.

Keywords: cobalt, molybdenum, utilization, catalysts.

Introduction

Compounds of cobalt and molybdenum, in particular, their oxides are used in many industries: chemical, petrochemical, metallurgical and mechanical engineering. Molybdenum (VI) oxide is also widely used as catalysts for various organic transformations, and as products for obtaining the metals themselves and their compounds [1]. Molybdenum (VI) oxide is also widely used as catalysts for various organic transformations, and as products for obtaining the metals themselves and their compounds [1]. Consequently, obtaining these substances from spent cobalt-molybdenum catalysts seems to be very urgent.

Cobalt - molybdenum-containing catalysts are widely used in petrochemical and chemical technology for hydrogenation, hydrocracking, oxosynthesis and many other processes. Residues and wastes of such chemical industries in most cases contain small amounts of cobalt

and noticeable amounts of organic substances, and amount to tens of thousands of tons per year [3].

The possibility of such processing will significantly reduce the amount of waste, which will improve the ecology of industrial areas, as well as return valuable cobalt and molybdenum compounds to technological cycles.

For this, it is necessary to develop a technology for the utilization of cobalt-molybdenum catalysts and to study the possibility of obtaining molybdenum oxides from spent molybdenum-containing catalysts.

To achieve this goal, the properties of molybdenum oxides and carbides were studied, which showed the existence of certain phases, the composition of which changes in narrow temperature ranges. Thus, molybdenum oxide can exist both in the α - phase (molybdenum oxide (IY)) and δ - phase (molybdenum oxide (YI)), γ - phase, β - phase, χ - phase (oxides of intermediate composition).

Based on the properties of molybdenum compounds, it was decided to use the method of differential thermal analysis. Using this method, it was necessary to determine the temperature regimes for obtaining substances from the initial sample. The spent molybdenum catalyst is a black oily powder with a pungent unpleasant odor, which is a mixture of molybdenum oxides and organic, aliphatic compounds.

Differential thermal analysis was carried out on a derivatograph of the PES system, according to four curves recorded on calibration paper in the axes: temperature (with a step of 100°) and weight loss (with a step of 5%). As a result of the analysis of derivatograms, an assumption was made about the possibility of the formation of several different substances, at temperatures of 380°C, 540°C, 700°C, which may correspond to molybdenum oxides.

The firing of the spent molybdenum-containing catalyst was carried out in a muffle furnace at three temperatures, lasting about two hours and gave the following results:

1. At T = 380°C, a gray substance was obtained.
2. At T = 540°C, a greenish-gray substance was obtained.
3. At T = 700°C, a yellow substance was obtained. White needle-like crystals were removed from its surface.

Then the experiment was repeated. Its difference was that the sample was placed in an already heated furnace at temperatures of 380°C, 540°C, 700°C. The phenomenon of "thermal shock" was observed, however, as a result of the experiment, substances of a similar color were formed. So the question of the possibility of the formation of molybdenum carbides under the given firing conditions is still open.

The substance obtained at 380°C resembles molybdenum oxide (IY) in its properties - small crystals of violet-gray color. The substance obtained at 540°C resembles in its properties the oxide of variable valence (Mo_4O_{11}). The substance obtained at 700°C resembles molybdenum oxide (YI) in its properties - yellowish-white crystals under a microscope, representing a mixture of transparent needles and opaque spherical agglomerates. White crystals resemble molybdenum oxide monohydrate (YI) (MoO_3*H_2O) in properties.

To identify the obtained substances and the possibility of detecting molybdenum carbides in the products of firing, we carried out a spectrophotometric analysis. The processing of IR spectra for the structural groupings of atoms and absorption bands confirmed that the substances obtained in the process of firing are molybdenum oxides. In addition, spectrophotometric analysis showed that the substances obtained by firing with a gradual increase in temperature and "thermal shock" are of the same nature, and the question of molybdenum carbides remains open. However, the possibility of utilization of spent molybdenum-containing catalysts is not limited to the production of oxides and carbides of molybdenum. Currently, the possibility of processing oxides and carbides into a valuable strategic metal - molybdenum - is being studied.

The object of the study was the catalysts of four grades of the following composition (table).

Table. Elemental composition of catalysts

Elements, %	Catalyst 1	Catalyst 2	Catalyst 3	Catalyst 4
C	3.7	9.8	10.6	
O	33.2	24.5	32.1	42,71
Al	27.5	13.6	20.1	39,7
Si	–	0.9	1.9	
V	–	2.9	–	
Fe	–	10.9	24.6	0,06
Ni	–	4.3	2.5	
Co	3.8	–	1.8	3,54
Mo	31.8	39	35.8	13,5
Ca	–	0.87	–	

These catalysts contain up to 30-40% molybdenum compounds.

The method of decomposition of spent catalysts combined in itself: the process of melt formation based on the spent catalyst with its subsequent dissolution. For this, it is important, on the basis of the physicochemical properties of the catalyst components, to correctly select the conditions for carrying out the sintering and dissolution processes: temperature, time, reagents and their ratio. The intensity of its dissolution will be determined by the surface area of the

contact between the phases and the structure of the melt: the degree of porosity and pore size, the size and shape of grains, and so on.

Weighed portions of the test specimens are placed in a quartz crucible and loaded into an incineration furnace, where the crucibles are uniformly heated to 900°C. During the experiment, heat and weight effects are recorded.

The method of decomposition of the spent catalyst combined in itself: the process of formation of a melt based on the spent catalyst with its subsequent dissolution.

Samples of blue catalyst 4 were fused in porcelain crucibles with sodium hydroxide in a mass ratio of 1:6 and a temperature of 330°C.

Further, the melt is dissolved in water, followed by boiling with 3% hydrogen peroxide solution for 10 minutes, which ensures complete oxidation of molybdenum in solution from trivalent to pentavalent.

Then, the aqueous extract was filtered on a vacuum pump and the pH of the solution medium was measured.

Thus, on the basis of the physicochemical properties of the components of the spent catalyst, the conditions for the process of its decomposition were selected: temperature, time, reagents and their ratio.

There are several types of roasting: calcination, oxidizing, chlorinating, reducing and sintering, which are named from the nature of the occurring chemical phenomena.

Using high-temperature firing, in this work, the spent catalyst is sintered with sodium hydroxide at a temperature of 330°C, as well as the conversion of molybdenum and cobalt compounds obtained as a result of precipitation into the compounds we need: cobalt and molybdenum oxides.

Results and discussion

When developing a method for the joint determination of molybdenum and cobalt in solution, it is necessary to take into account the following factors for determining the content of each element separately: the ability to form colored thiocyanate complexes in solution, their stability under various media, as well as the possibility of their extraction by organic solvents and the range of their determination. All stained thiocyanate complexes dissociate significantly. Due to the stepwise formation of thiocyanate complexes and their different colors (for the same cation), it is imperative that the concentration of the reagent be the same in the test and standard solutions. For the possibility of joint extraction of thiocyanate complexes, organic solvents are used that do not mix with water; they dissolve the colored thiocyanate complexes well, removing

them from the aqueous layer. For the extraction of colored thiocyanates, diethyl ether, amyl alcohol, acetone, and other solvents are most often used.

Deposition conditions: the product of ion activities in powers corresponding to stoichiometric coefficients must be greater than the table value. Therefore, the pH value corresponding to precipitation does not remain strictly defined; it depends on concentration, temperature and other conditions and fluctuates within certain limits [4]. Thus, it is possible to separate cobalt compounds from molybdenum compounds in solution by adjusting it to a certain pH value, gradually increasing the pH value by adding alkali. The method is based on the fact that when metal hydroxides are precipitated at low pH values, hydroxides of other metals formed at higher pH values are not yet precipitated.

In order to obtain information about the object of research, differential thermal, IR spectroscopic analysis of green and blue granules of the spent cobalt-molybdenum catalyst was carried out.

The formation of endothermic effects in the temperature range 100–160°C on the DTA curves can be explained by the removal of adsorbed moisture from the samples under study during heating.

According to the obtained results of differential thermal analysis, it can be assumed that the green granules are crystalline hydrate, when heated, the removal of crystallization water occurs, accompanied by a rearrangement of the structure of the substance. To confirm the assumption that the green granules are crystalline hydrate, IR spectroscopic analysis of the green and blue granules of the spent catalyst was performed.

The IR spectrum of green granules of the spent catalyst showed in the region of 3600-3200 cm-1 the presence of a number of bands (3095, 3300, 3500) inherent in the stretching vibrations of O-H and at 1630-1600 cm of the band characteristic of the bending vibration of H-O-H [5]. Whereas the IR spectrum of blue granules in the region of 3600-3200 cm-1 has only one broad band, the formation of which can be explained by the adsorption capacity of the substance. In the region of 1200-1000 cm-1 of the IR spectrum of green granules, a band of medium intensity is observed, it is absent in the IR spectrum of blue granules.

To explain this phenomenon, it was proposed to heat green and blue granules at temperatures of 120, 350, 600°C for two hours. When the blue granules were heated at temperatures of 120, 350, 600°C, no changes in the structure were observed. For green granules, on heating at temperatures of 120, 350, 600°C, the structure of the substance changed, for example, at a temperature of 350°C, partial amorphization of the structure was observed and a decrease in the intensity of the band in the range of 1100-950 cm-1, at 600°C the band

completely disappeared and the structure of the substance became completely amorphous [5]. On the basis of the obtained results of differential thermal and IR spectroscopy, it was concluded that green granules are crystalline hydrate, which, when heated from 400 to 600°C, completely loses water. The loss of water in the granules is characterized by a color change from green to blue.

The data obtained correlate with the properties of cobalt compounds, which indicate that during heating in air in the range of 400-600°C, cobalt (II) oxide transforms into cobalt (II, III) oxide with a change in the color of olive green to blue [6].

Conclusions

1. The optimal conditions for the preparation of the utilization catalysts were selected: fusion with sodium hydroxide in a mass ratio of 1:6 at a temperature of 330°C for 3 hours, followed by dissolution of the melt with water.
2. The obtained melts were investigated for the presence of molybdenum compounds: by the method of IR spectroscopic analysis; by the method of differential thermal analysis, by the method of X-ray structural analysis; by the method of photocolorimetric analysis.
3. A method for the determination of molybdenum in the solutions under study has been worked out, based on the joint extraction of thiocyanate complexes of cobalt and molybdenum in the presence of potassium thiocyanate and tin (II) chloride. A common extractant, acetone, was selected for joint extraction.

References

[1] Chemical technology of inorganic substances: In 2 b. B. 2. Textbook. allowance. T.G. Akhmetov, R.T. Porfirieva, L.G. Gaisin and others M.*: High. sch.* **2002**. 533P.

[2] Chemical encyclopedia. T1. *M.: Soviet encyclopedia.***1990**. 671P.

[3] Lysanova G.V. Physicochemical study of oxide and hydroxide compounds of molybdenum: *Abstr diss…cand. tech. sci:* 02.00.16. M. **2000**. 16P.

[4] Analytical chemistry: textbook for universities. V.I. Gorokhovskaya, V.F. Sopin, G.K. Budnikov. *Kaz. st. tech. un-ty. Kazan.* **2000**. 464P.

[5] Khatsrinova Yu.A., Khatsrinov A.I. Method for separating cobalt and molybdenum in spent catalysts. Kazan Technological University Bulletin. *Kazan. KSTU.* **2012**. V.15. №8. P.46-50.

[6] Khatsrinova Yu.A., Khatsrinov A.I. Investigation of the composition of the spent molybdenum-containing catalyst. *Kazan Technological University Bulletin.* **2013**. V.15. №8. P.46-50.