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CATALYSTS OF HYDROPROCESSES IN OIL REFINING. PRODUCTION AND REGENERATION

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Aluminum—nickel— and aluminum—cobalt—molybdenum (ANM and ACM) catalysts are widely used for hydrotreating, hydrocracking, hydroisomerization, and dewaxing of crude oil cuts. Their production, in a world volume of approximately 90,000 tons/year, involves the use of a large amount of metal salts, acids, and bases, resulting in the formation of wastewaters and harmful atmospheric emissions.

The necessity of improving the environmental conditions, especially in regions where oil refineries are located, has stimulated interest in developing low-reagent methods of manufacturing catalysts and supports, reducing wastes and atmospheric emissions, and utilizing spent catalysts, included by almost all countries in the list of potentially dangerous wastes. Nickel(cobalt)-containing catalysts must be buried in specially enclosed bunkers to prevent contamination of ground waters.

The fundamental directions in developing low-waste technology for manufacturing ANM (ACM) catalysts and methods of utilizing these catalysts spent in different processes are examined below.

TABLE I

Indexes	Method of manufacturing AAO		
	reprecipitation		with low-waste technology
	nitrate	aluminate	
Consumption			
caustic soda (commercial-grade), kg/ton	1418	100	–
acid, kg/ton			
sulfuric	–	1200	–
nitric	4320	25	150
steam, GJ/ton	226.8	189	84
electric power, kwh/ton	3680	3800	1500
water, m^3/ton			
tap	400	400	50
chemically purified	300	–	30
fuel, ton of theoretical standard fuel/ton	0.30	0.30	
Cost of 1 ton of AAO, thousands of rubles	25	21	13

Note. For manufacturing 1 ton of product, 1100 kg of alumina was processed with each method.

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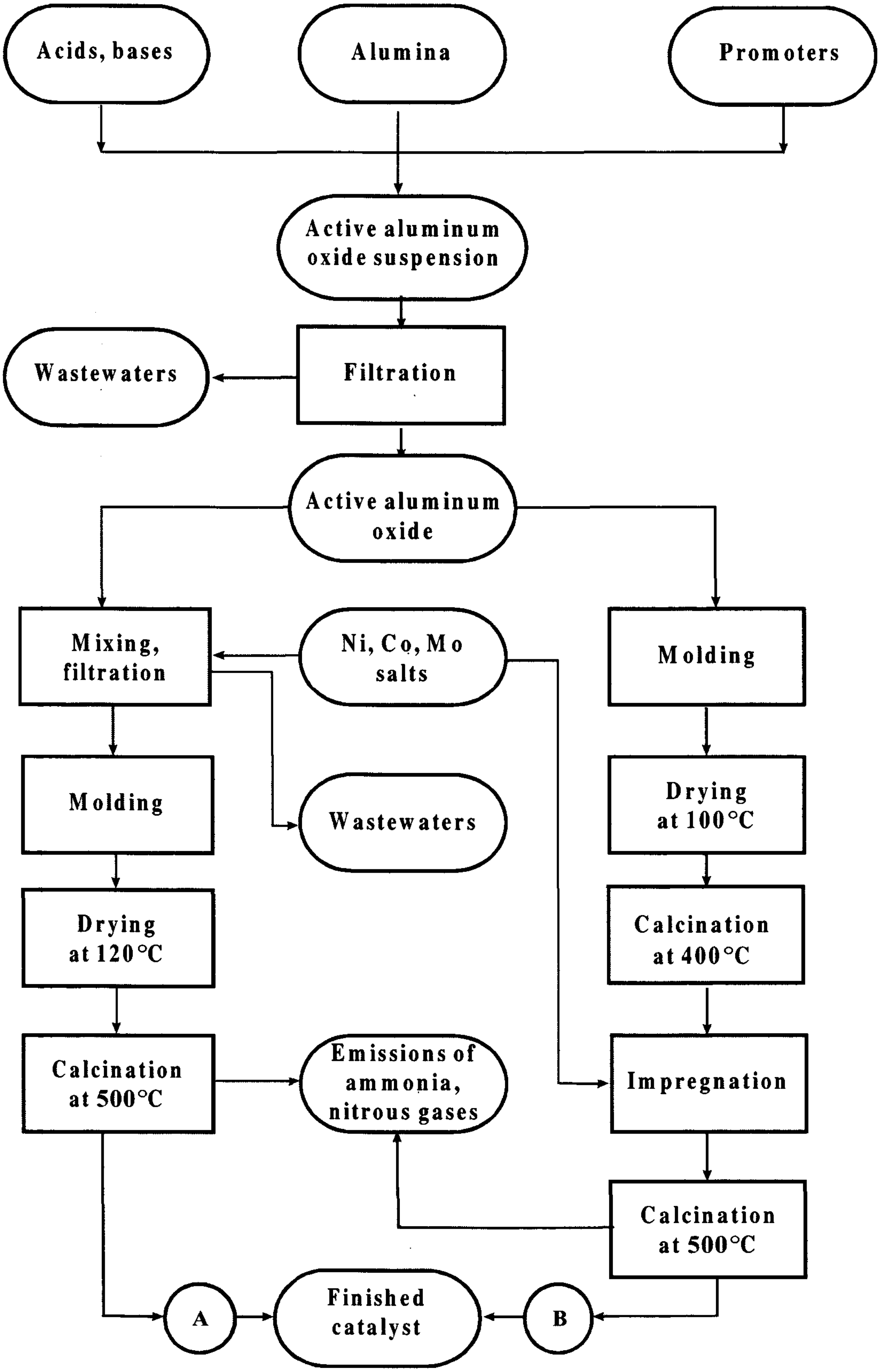

Fig. 1. Flow chart of manufacture of catalysts by methods of reprecipitation (A) and impregnation (B).

MANUFACTURE OF ACTIVE ALUMINUM OXIDE (AAO)

This stage of manufacturing catalysts is the basic source of wastewaters. The method of manufacturing AAO by reprecipitation of alumina with production of aluminum hydroxides of the boehmite-pseudoboehmite and bayerite types is the most widespread [1 – 3]. The following variants are possible:

basic (aluminate) — precipitation from basic solutions by acids or acid solutions of salts;

acid (nitrate) — precipitation from acid solutions of aluminum salts with solutions of bases.

The consumptions of feedstock and reagents for manufacturing 1 ton of AAO are reported in Table 1. Almost all of the reagents used in the form of solutions of salts (300 – 500 m^3 per ton of support obtained) are discarded as wastewaters and require utilization and consequently additional capital investments, which increases the cost of the AAO by 30 – 40%.

The drawbacks of these methods are: high consumption of acids and bases; multistage character of the process and consequently high losses of target product in filtration and washing; formation of a large amount of wastewaters containing the acids, bases, and their salts; high power consumption.

To eliminate these drawbacks, a low-waste technology for manufacturing AAO by thermal dispersion of alumina trihydrate has been intensively developed in the past ten years. This process simultaneously includes processes of disordering of the crystal structure, dehydration and dispersion at a high rate of heating particles of gibbsite [4 – 6].

Amorphized ρ-Al_2O_3 with qualitatively new properties is the product of thermal dispersion. In particular, it can swell in water with formation of hydrated aluminum oxide residues which have plasticity and the capacity to be molded into strong granules. The conditions of thermal dispersion are selected so that the AAO obtained has almost the same chemical composition as AAO manufactured by reprecipitation.

Conducting heating and calcination at 350 – 800°C for 0.2 – 10 sec is recommended in [7], and initially heating an aqueous suspension of hydrargyllite at 95 – 100°C and then treating it with heat at 100 – 250°C in the presence of a stabilizer, barium nitrite, are recommended in [8]. Heating diaspore in a vacuum at 300 – 1000°C is proposed in [9], and heating in a fluidized bed and passage through a series of units, each at a temperature 100 – 120°C higher than in the preceding unit, is suggested in [10].

Manufacture of AAO by thermal dispersion includes the following operations: grinding and drying, high-temperature heating, hydration, washing, and plasticization of the alumina, yielding AAO hydrogel. According to the data in Table 1, consumption of acids is decreased by 8 – 25 times, consumption of water is

TABLE 2

Criterion	Method of utilization	
	reactivation	recovery of metals
Total sodium content, %	<3.5	>3.5
Strength coefficient, N/mm	>15	<15
Specific surface area, m^2/g	>105	≤105

TABLE 3

Indexes	Catalyst		
	GKD-205	GP-526	GO-117
Strength coefficient, N/mm	18	11	9
Specific surface area, m^2/g	62	128	105
Content, wt. %			
molybdenum	13	12	21
nickel	4	3	7.5
sodium and iron	3.6	1.5	2.4

reduced by 5 – 10 times, use of caustic soda is eliminated, formation and dumping of wastewaters in sewers are reduced, the productivity of the plant is increased, and the cost of the AAO is reduced by 35 – 45% with the low-waste technology in comparison to reprecipitation.

MANUFACTURE OF CATALYSTS BASED ON AAO

In most cases, domestic catalysts are based on AAO manufactured by reprecipitation by mixing it with a suspension of active metal (molybdenum, nickel, or cobalt) salts and a promoter solution [1, 11]. The compound obtained is filtered several times, then molded, dried, and calcined at high temperature (Fig. 1). Wastewaters with carcinogenic nickel (cobalt) and molybdenum compounds are formed, and nitrogen oxides, ammonia, and other compounds are emitted into the atmosphere as a function of the chemical composition of the catalyst.

Our technology for manufacturing AAO catalysts includes the following basic operations: fabrication of the support — AAO — by thermal dispersion; addition of promoters to the support to regulate its structure; mixing of pellets of AAO with active metal salts used in amounts calculated from the defined content in the catalyst; molding of the catalytic compound into granules; drying and calcination of the granules; scrubbing of harmful compounds from the gases.

In implementing this technology, no wastewaters with harmful metal contaminants are formed. They were previously formed during filtration of the catalytic mass due to the use of a solution of active metals with a 1.5 – 2-fold excess of nickel (cobalt) and molybdenum salts.

Another advantage of this technology is removal of nitrous gases, ammonia vapors, and sulfur oxides from the calcination gases.

UTILIZATION OF SPENT CATALYSTS

Our studies demonstrated the inhomogeneity of the physicochemical properties of spent catalysts. Criteria were developed for selecting the method of utilization (Table 2) and used to study spent hydrotreating catalysts (Table 3).

It is not useful to restore the activity of catalysts due to worsening of their properties; for this reason, recovery of the metals in pure form or as salts is recommended. The spent catalyst undergoes acid treatment to destroy the structure. The amount of wastes formed should be minimal.

Extraction of molybdenum, nickel, and aluminum, as well as iron and sodium, from a spent catalyst by treating it with mineral acids of different concentration was investigated. According to the data in Table 4, the concentrated acids are in the following order with respect to the increase in the degree of extraction of these metals, the ones of greatest interest:

$$HCl > H_2SO_4 > HNO_3$$

The concentration of the dilute acids significantly affects the amount of metal extracted (Table 5). When the concentration increases, the degree of extraction of the metals, especially nickel, increases [11 – 14]. The degree of extraction of nickel almost does not change, but extraction of aluminum increases to 88% when the temperature is increased to 80°C.

TABLE 4

Metal	Degree of extraction (%) from spent catalyst with solutions of concentrated acids		
	HNO_3	H_2SO_4	HCl
Nickel	67	83	95
Molybdenum	15	25	28
Aluminum	35	27	38
Iron	100	92	100
Sodium	100	100	100

However, the molybdenum contained in the catalyst is poorly extracted by acid treatment. For this reason, the effect of ammonium compounds — sulfate and hydroxide— on recovery of molybdenum was investigated. The degree of extraction increases by almost 2 times for nickel, by 1.5 times for molybdenum, and by almost 2 times for aluminum in extraction with ammonium sulfate when the temperature is increased from 40 to 120°C (Table 6). The extractant:catalyst ratio also affects the extractability of molybdenum and aluminum in treatment with ammonium sulfate or hydroxide.

With a six-fold excess of ammonium compounds, the degree of extraction of molybdenum increases by 1.5 times. Solutions of a mixture of nickel and aluminum sulfates and a solution of ammonium paramolybdate are obtained (Fig. 2). The concentration of the latter is 200 g/liter in treatment of GO-117 catalyst and 120 g/liter in treatment of GKD-205 catalyst. For this reason, evaporation is recommended for separating the pure product. After this, "flakes" of ammonium paramolybdate precipitate out of the solution when the temperature is decreased.

For the best extraction of metals, spent catalysts should thus be successively treated with concentrated sulfuric acid at 80°C and ammonium compounds and then the paramolybdate solution should be evaporated to a concentration of 450 – 500 g/liter followed by crystallization. It is preferable to use ammonium hydroxide for extraction of molybdenum.

Based on the results of studying the different methods of separation of pure ammonium paramolybdate, technology was selected which includes the stages of two-stage evaporation and crystallization followed by centrifugation. Various reagents can be used for separating the other components — nickel and aluminum, and for initial decomposition of structures of the Ni—Al—Mo type or their derivatives. The metal salts obtained can be used for production of fresh catalysts.

The spent catalyst is contaminated by coke deposits and iron and sodium. To remove the coke, calcination at 500°C is recommended. After this, the catalyst is crushed in a ball mill to a particle size of 10 – 15 μm, then treated with a three-fold excess (by volume) of sulfuric acid while stirring and heating to 80°C for 6 h.

The mixture is allowed to settle, the sediment is separated, and ammonium hydroxide in a five-fold excess (by volume) is poured over it while stirring and heating to 60°C for 8 h to remove harmful substances. The sediment is washed with water and discarded in a dump. The solutions formed after treatment with sulfuric acid and washing with water are mixed and allowed to stand, then used for production of fresh catalyst [14, 15].

The solution obtained contains less than 3.2% $NiSO_4$, 58% $Al_2(SO_4)_3$, and 2% $(FeNa_2)_xSO_4$, so that it is necessary to carefully wash the aluminum hydroxide cake with water in filter-presses for preparation of fresh catalyst.

TABLE 5

Metal	Degree of extraction (%) with acids of different concentration						
	HCl, %		HNO_3, %		H_2SO_4, %		
	18	40	12	43	32	66	98
Nickel	23	41	15	35	42	54	83
Molybdenum	22	26	10	12	20	20	25
Aluminum	10	13	8	18	7	15	27

TABLE 6

Metal	Degree of removal (%) by extraction with ammonium sulfate at, °C				
	40	60	80	100	120
Molybdenum	46	54	62	67	60
Aluminum	28	40	53	53	50
Nickel	–	1	2.3	2.3	2.3

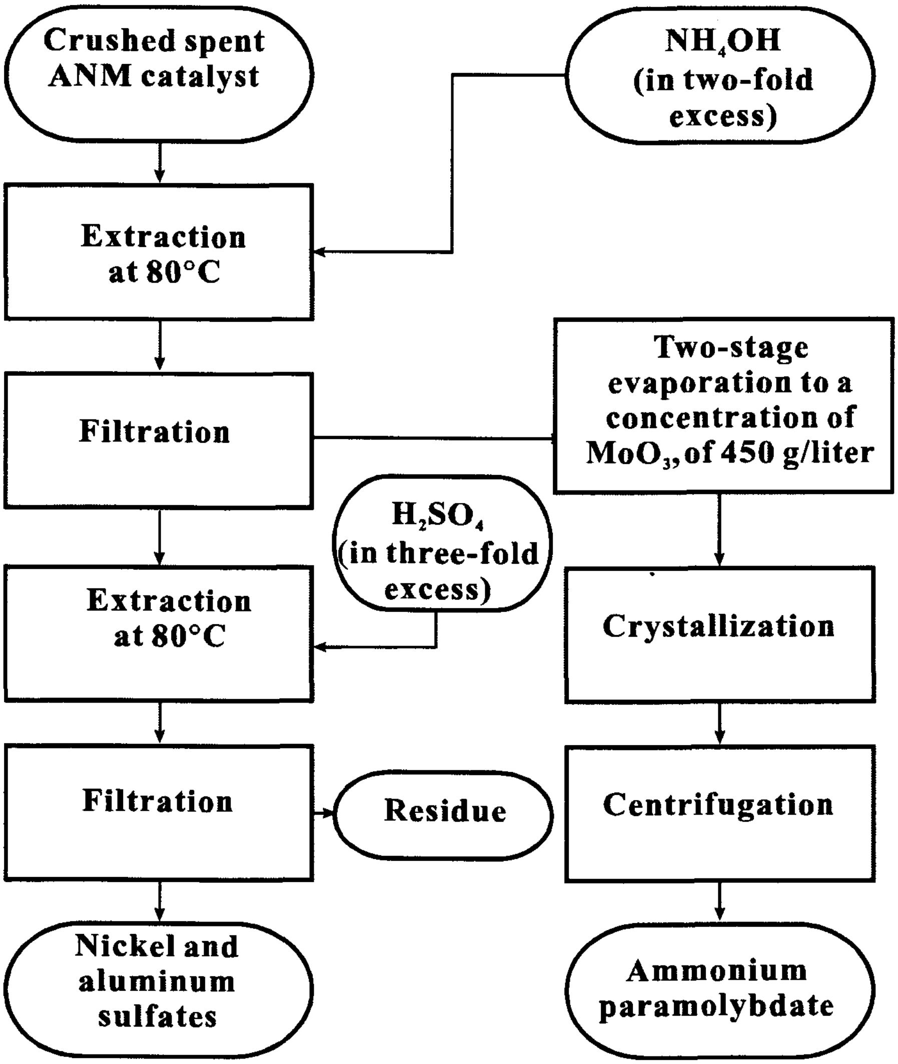

Fig. 2. Diagram of recovery of metals from spent catalysts.

After treatment with ammonium hydroxide, the solution is evaporated in two stages to a concentration of molybdenum trioxide of 150 and 450 g/liter, respectively. After this, it is crystallized and centrifuged. The ammonium paramolybdate obtained has a degree of purity of up to 93 wt. %. The coke, iron, and sodium impurities in it are less than 1.2 wt. %, and it contains residual amounts of nickel and aluminum.

The complex technology for production and use of ANM (ACM) catalysts comprises the following fundamental stages:

- synthesis of AAO with low-waste technology;
- preparation of the catalytic compound by mixing the initial reagents;
- drying and calcination of the finished catalyst;
- loading the catalyst in the industrial plant reactor;
- regenerating the catalyst and using it again in the process;
- extracting metal salts from spent catalysts, recycling them for production of fresh catalysts.

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