OBTAINING HETEROGENEOUS CATALYSTS FOR ACETONITRILE SYNTHESIS

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Abstract. *This article discusses the study of the properties of heterogeneous catalysts for the synthesis of acetonitrile. The process of acetylene condensation with ammonia in the presence of catalysts based on cadmium fluoride (KFA-1, KKFA-1, KFA-2, KCA-1) was studied. The condensation of acetylene with ammonia in the presence of cadmium fluoroaluminum catalysts was studied. It was found that the KFA catalyst stabilizes after the first cycle of operation, and the yield of acetonitrile decreases to a minimum and is from 5.0 to 10.0%. The main products of the reaction are mixtures of pyridine bases, among which 2- and 4-methylpyridines predominate. It was found that as the catalyst operates, its activity gradually decreases. The removal of metallic cadmium from the catalyst is observed.*
Keywords: *acetylene, ammonia, acetonitrile, catalysis, catalytic system, ammonolysis.*

INTRODUCTION. Wide industrial application of acetonitrile is delayed due to acetonitrile from more accessible compounds and selection of active catalysts, lack of cheap and convenient methods for its production. Therefore, the creation of new synthesis methods with high selectivity and productivity is an urgent task [1-2]. Acetonitrile is a universal solvent for many organic and inorganic salts, oils, resins, nitrocellulose, esters, acids, celluloid, alkaloids, polymers and other compounds. It is used in the production of amines, acid amides and pesticides, and is also used as a component of azeotropic distillation, selective extraction as a solvent in many processes. The first syntheses of acetonitrile and pyridine bases from acetylene and ammonia are given in the works of the famous chemists Meyer, Ramhay and Dewar [3-5], who, passing a mixture of acetylene with ammonia or hydrocyanic acid without a catalyst into a hot tube, obtained acetonitrile, a mixture of nitrogen-containing bases, etc.

The study of the condensation reaction of acetylene with ammonia was carried out at the beginning of the 20th century by the famous Russian organic chemists Chichibabin A.E. and Moshkin P.A., who, passing a mixture of acetylene with ammonia over catalysts containing oxides of aluminum, chromium, iron, isolated acetonitrile, a mixture of pyridine bases, ethylamines, resin, etc. [6, 7]. Japanese researchers [8] studied the condensation of acetylene with ammonia in the presence of aluminum oxide promoted with alkali metal salts and found that this catalyst has sufficient selectivity in the formation of acetonitrile. They studied in detail the influence of various factors on the course of the process. Based on the data obtained, it was established that the rate-limiting stage of the reaction is the formation of acetonitrile during the interaction of adsorbed acetylene with ammonia on areas of the catalyst surface that do not have acidic properties. Side reactions - the formation of hydrocyanic acid, as well as the decomposition of acetylene and ammonia occur on the non-acidic surface of the catalyst. At the same time, the polymerization reaction and the formation of pyridine bases occur on the acidic surface.

According to other authors [9], the catalyst has two types of acid centers: acetonitrile is formed on the first, and pyridine bases, resins, and other by-products are formed on the second. By condensing acetylene with ammonia in the liquid phase, Reppe [10] obtained 2-methyl-5-ethylpyridine with a 75% yield with a small amount of by-products, acetonitrile, etc. It was found that alkali metal chlorides do not accelerate the reaction of acetonitrile formation, but suppress side reactions and, consequently, the yield of acetonitrile increases.

American scientists [11] obtained acetonitrile with a 60% yield by condensing acetylene with ammonia at 440-550°C in the presence of molten zinc chloride. Various systems of molten metal chlorides were used to synthesize acetonitrile. The most active system was found to be the one containing molten zinc chloride. The authors found that increasing the acetylene:ammonia ratio from 1:1 to 7:1 leads to a decrease in the yield of acetonitrile due to side reactions.

The synthesis of acetonitrile from acetylene and ammonia in the presence of a heterogeneous catalyst was studied.

Acetonitrile as a starting material in various syntheses can be obtained in several ways [2]:

a) in industry, acetonitrile is obtained by ammonolysis of acetic acid at 300 - 400°C, using a small excess of ammonia;

b) in the laboratory, acetonitrile is obtained by dehydration of acetamide under the action of P_2O_5.

Currently, in Uzbekistan, the most promising industrial synthesis is the synthesis of acetonitrile from acetylene and ammonia.

By selecting selective, high-performance catalysts and process conditions, it is possible to achieve a high yield of acetonitrile, an important product of basic organic synthesis [12 - 14].

MATERIALS AND METHODS. As noted above, zinc oxide catalyzes the reaction of acetonitrile formation from acetylene and ammonia. In order to obtain comparative data, we prepared a series of catalysts [15] in which the zinc oxide content varied from 3.0 to 20.0% by weight. When studying the process of acetylene condensation with ammonia in the presence of a zinc-aluminum catalyst (CA-1) containing 20.0% zinc oxide, the formation of acetonitrile passes through a maximum (Fig. 1). A further increase in the ZnO content in the catalyst leads to a decrease in activity. When passing a mixture of acetylene with ammonia at a ratio of 1:2 vol., at a rate of 150 l/l·cat·hour at temperatures of 400 - 420 °C, acetonitrile is obtained with a yield of 58.0% of the theory. Zinc-aluminum catalyst CA-1 operates in the temperature range of 380 - 450°C for 8 hours. After that, it significantly loses its activity. The conversion of acetylene in the presence of this catalyst does not exceed 70%. Carrying out the process at relatively elevated temperatures (450°C and above) leads to a decrease in the selectivity of the catalyst. If at temperatures of 380 - 420°C a condensate is formed, consisting mainly of acetonitrile, then with an increase in temperature, mixtures of nitrogen-containing heterocycles 2-methylpyridine, 4-dimethylpyridines, etc. appear in the catalyst.

RESULTS AND THEIR DISCUSSIONS. Based on preliminary studies, we came to the conclusion that zinc oxide on aluminum oxide does not meet the requirements for industrial catalysts in the synthesis of acetonitrile.

Further studies on the synthesis of acetonitrile from acetylene and ammonia were carried out in the presence of a chromium-aluminum catalyst (XA-I). The study of this catalyst was carried out in the temperature ranges of 280-480°C. Chromium-aluminum catalysts are widely used in industry and their use in the synthesis reaction of acetonitrile is of undoubted interest. It is known that catalysts based on chromium oxide are used in dehydrogenation reactions. The reaction of

acetonitrile formation from acetylene and ammonia also refers to dehydrogenation processes, therefore, chromium oxide was used by us as a contact in this reaction.

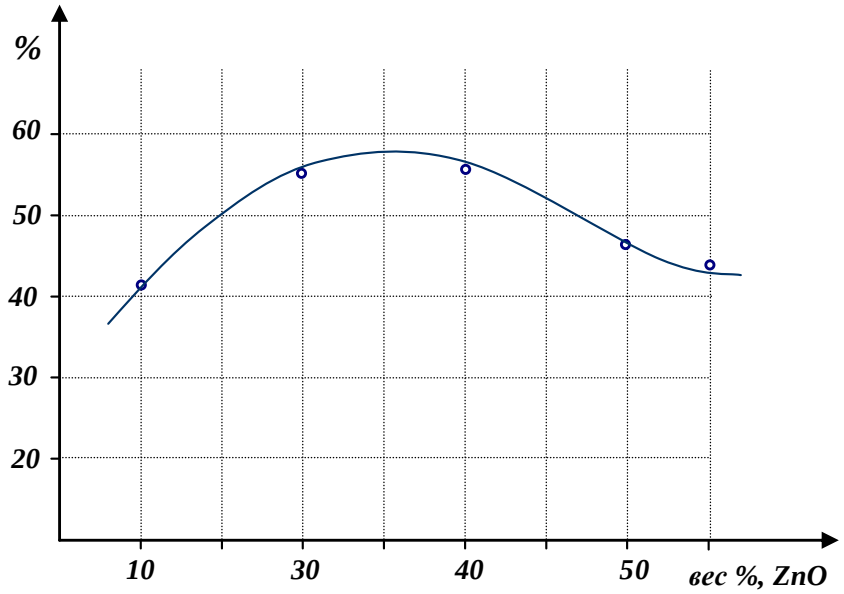

Fig. 1. Dependence of the CH_3CN yield on the ZnO content in the catalyst

The study examined the effect of temperature, the volume ratio of ammonia to acetylene, the space velocity, etc. on the acetonitrile yield. Analysis of the catalysate showed that in the presence of an aluminochromium catalyst, acetonitrile is mainly formed from acetylene and ammonia. In this case, the process temperature decreases to 60 - 140 °C compared to known catalysts, such as zinc oxide or aluminum oxide. The catalyst, without reducing its initial activity, operates for 18 hours, after which it requires regeneration.

The effect of temperature was studied in the ranges of 300 - 420 °C (Fig. 2). As can be seen from the data in Fig. 2, increasing the temperature to 360 °C promotes the formation of acetonitrile. A further increase in temperature leads to a decrease in the yield of acetonitrile due to by-products (formation of methylpyridines, decomposition of acetylene, etc.).

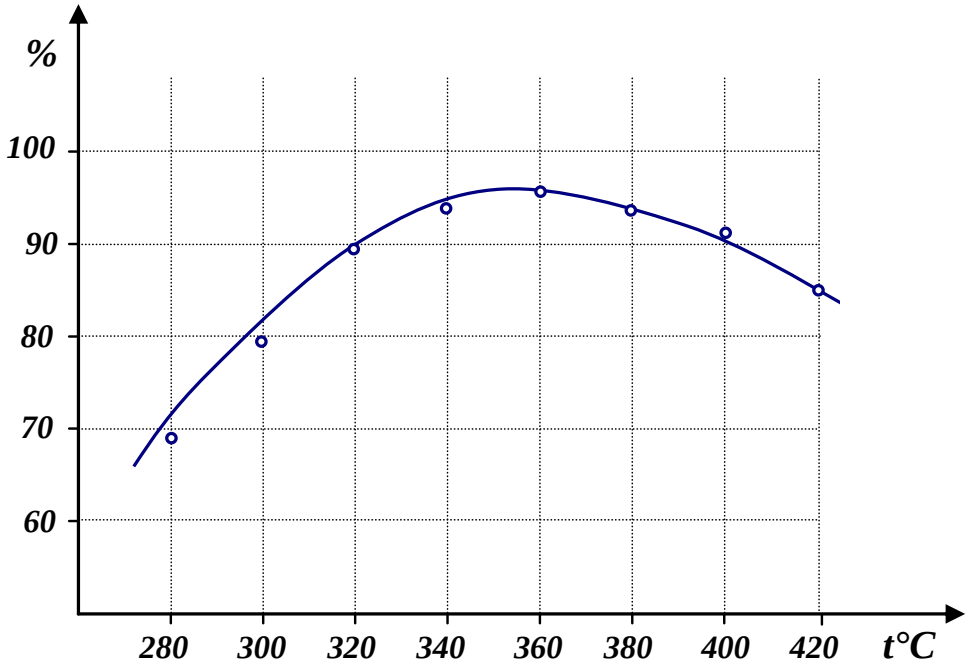

Fig. 2. Dependence of acetonitrile yield on temperature (in %, per passed acetylene)

The process of acetylene condensation with ammonia in the presence of catalysts based on cadmium fluoride (KFA-1, KKFA-1, KFA-2, KCA-1) was studied. The condensation of acetylene with ammonia in the presence of cadmium-fluoro-aluminum catalysts was studied. The reaction was carried out in the temperature range of 270-360 °C, with the ratio of acetylene: ammonia = 1:2.

Table 1

Main performance indicators of the KFA-1 catalyst

№	Time from the beginning of the experiment, hours	Tempe-rature, °C	Acetylene conversion%	Composition of liquid products, % by weight			
				Acetonitrile	2-methyl-pyridine	4-methyl-pyridine	Higher pyridines
1	**2**	**3**	**4**	**5**	**6**	**7**	**8**
1.	8	260	42,0	72,0	15,0	8,0	3,0
2.	16	270	54,0	66,0	18,0	10,0	5,0
3.	26	280	65,0	53,0	26,0	14,0	6,0
4.	43	292	74,0	52,0	34,0	12,0	1,0
5.	48	304	78,0	46,0	36,0	13,0	3,0
6.	60	310	83,0	56,0	26,0	14,0	2,0
7.	72	320	84,0	54,0	28,0	13,0	4,0
8.	86	360	86,0	48,0	34,0	12,0	5,0

In order to determine the service life of the catalyst and establish the main process parameters, a series of experiments were performed on one sample of the catalyst (KFA - 1). The experiments were carried out on a laboratory setup in a stainless steel reactor with a 100 cm bulk volume of the catalyst at a total space velocity of 180-200 l/l·cat·hour (Table 1).

As can be seen from the table, the conversion of acetylene at 260-280 °C is 42-65%. With an increase in temperature, the conversion of acetylene reaches 86%. The selectivity of acetonitrile formation with an increase in the selectivity of the process of formation of 2- and 4-methylpyridines.

It was found that the KFA catalyst stabilizes after the first cycle of operation, and the yield of acetonitrile decreases to a minimum and is from 5.0 to 10.0%. The main products of the reaction are mixtures of pyridine bases, among which 2- and 4-methylpyridines predominate.

As experimental data show, acetonitrile can be successfully synthesized in the presence of SKhKA catalysts. The use of zinc-chromium or cadmium-fluoro-aluminum catalysts in the synthesis of acetonitrile does not provide high conversion, selectivity, and other process parameters.

We used cadmium sulfate as a catalyst in the acetonitrile synthesis reaction. Of the cadmium compounds, cadmium sulfate is easily accessible and catalysts based on it are prepared in the usual way.

To select the optimal content of the active component (cadmium sulfate), which has the highest activity in the acetonitrile synthesis reaction, we conducted a series of preliminary experiments with various samples, differing in the content of cadmium sulfate. All experiments on the cadmium sulfate catalyst on aluminum oxide were carried out at a temperature of 300 - 400

°C, a volumetric gas mixture velocity of 350 l/l·cat·hour, a catalyst volume of 100 cm^3 and a constant ratio of acetylene : ammonia = 1:2.5 vol.

It was found that with an increase in the cadmium sulfate content in the catalyst to 30% by weight, the yield of acetonitrile passes through a maximum corresponding to a cadmium sulfate content of 20% by weight. A further increase in the cadmium sulfate content in the catalyst leads to a decrease in activity. Apparently, the observed maximum of activity corresponds to a monolayer surface coverage.

X-ray diffraction patterns of catalysts with a cadmium sulfate content from 5.0 to 30 wt. It was found that with a cadmium sulfate content of up to 20% by weight on the carrier, characteristic lines for cadmium sulfate were not detected in the X-ray diffraction patterns. In samples containing 20-30% cadmium sulfate, clear lines characteristic of cadmium sulfate crystals appeared.

Diffraction patterns of the cadmium sulfate catalyst were recorded at a temperature of 700°C. It was found that heating the catalyst to 700°C leads to phase changes. The cadmium sulfate catalyst obtained by calcination to 700°C exhibits approximately two times lower activity compared to catalysts obtained by calcination at 450°C. Further studies were conducted on a catalyst containing 20% cadmium sulfate calcined at 450 - 500 °C.

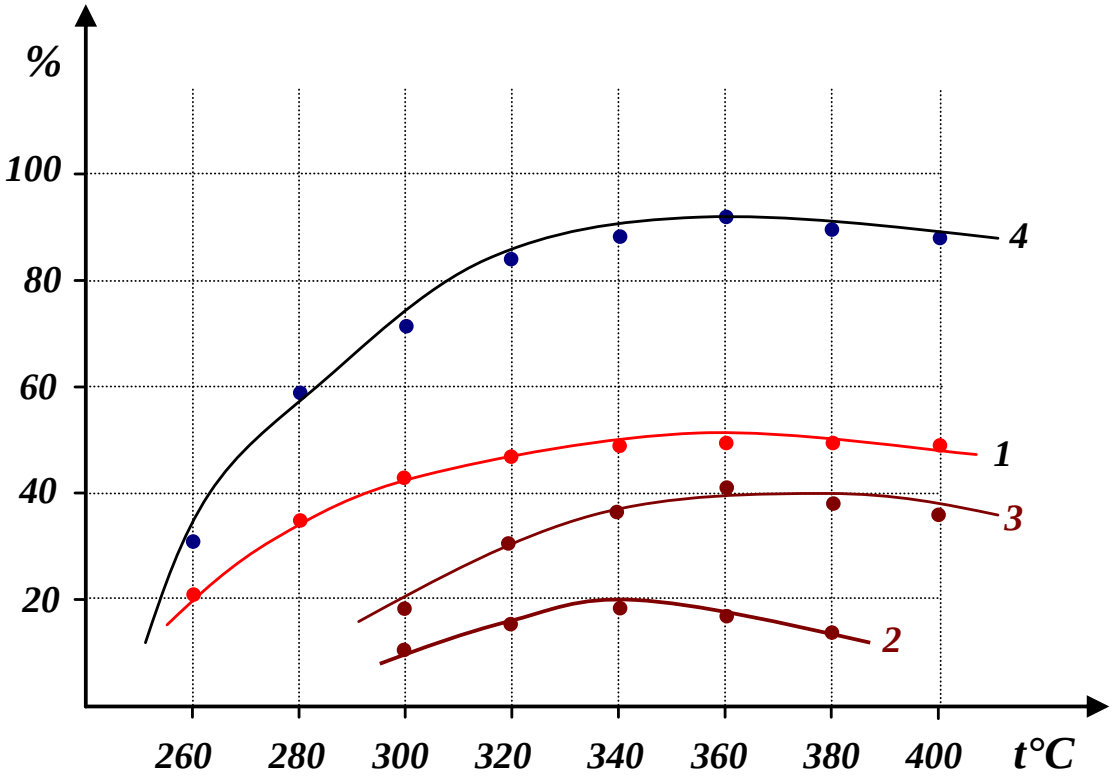

Fig. 3. Dependence of the yield of acetonitrile on temperature
1 – acetonitrile; 2 – 2-methylpyridine; 3 – 4-methylpyridine; 4 – acetylene conversion

The effect of temperature, space velocity, ratio, operating time and other factors on the yield of acetonitrile and the selectivity of the process was studied [16].The effect of temperature was studied in the temperature range of 260 - 400°C.

As can be seen from Fig. 3, with an increase in temperature from 260 to 360 °C, an increase in the yield of acetonitrile, as well as 2- and 4-methylpyridines, is observed. At 360°C, the yield of 2- and 4-methylpyridines reaches a maximum and is and 10.0%, respectively. Conversion of acetylene at 350°C is achieved up to 90%.

The change in the activity of the cadmium sulfate catalyst over time at a temperature of -340 °C, an acetylene: ammonia ratio of 1:3 and an acetylene volumetric flow rate of 75 l/l·cat·hour is shown in Table 2.

Table 2

Change in the activity of cadmium sulfate catalyst over time

№	Time from the beginning of the experiment, hours	Acetylene conversion, %	Composition of liquid products, reactions, %		
			Acetonitrile	2-methyl-pyridine	4-methyl-pyridine
1	**2**	**3**	**4**	**5**	**6**
1.	4	98,0	82,0	10,0	4,0
2.	8	94,0	80,0	14,0	3,0
3.	12	90,0	72,0	18,0	7,0
4.	16	82,0	68,0	21,0	10,0
5.	20	72,0	60,0	25,0	13,0
6.	24	67,0	54,0	27,0	16,0
7.	28	60,0	48,0	22,0	11,0

As can be seen from the data in Table 2, the activity of the cadmium sulfate catalyst for acetonitrile decreases over time, which is directly related to the removal of active centers, especially cadmium, by the flow of the initial reagents - acetylene and ammonia, which is proven by a decrease in the conversion of acetylene.

CONCLUSION. Based on the conducted studies, it can be concluded that the reaction of acetylene with ammonia has a complex nature. Regardless of the nature of the catalysts used, the reaction can be directed toward the formation of acetonitrile, or toward the formation of 2- and 4-methylpyridines. Among the studied zinc-chromium-cadmium-aluminum catalysts, sodium carbonate-promoted contact masses have a sufficiently high activity, selectivity and stability and they can be recommended for use on an industrial scale.

Thus, we studied the reaction of catalytic synthesis of acetonitrile from acetylene and ammonia.

REFERENCES

1. Paushkin Ya.M., Osipova L.V. // Advances in Chemistry. 1959. Vol. 28. Issue 3. pp. 237 - 264.
2. Mekhtiev S.D. Nitriles. Baku: AzGI. 1966. p. 466.
3. Devar T. Beso arche on the Picoline and Chinoline Bases. Proc. Roy.Soc. Long.
4. Chemistry of acetylene. Coll. ed. A.D. Petrov. Moscow: IL., 1954. pp. 205-206.
5. Meier R, Wasche H. Pyrosene Acetylene Codencation. Vegr., 1917, Vol. 50, pp. 423-441.
6. Chichibabin A.E. Syntheses using acetylene / ZhRFKhO, 1915. T.47. P.703-713.
7. P. Chichibabin A.E., Moshkin P.A. Condensation of acetylene with ammonia in the presence of aluminum oxide / ZhRFKhO, 1924. T.54. No. 3. P.611 - 624.
8. Murakami T., Shiba T. Synthesis of acetonitrile from acetylene and ammonia. T. Acetes 2nd Congress International Catalyses, Paris, 1960, V. 2. P 2472-2493.
9. Etnuro B., Sadao O., Kiochi H. Effect of the Alhali addition on the catalytic Proportioc of Alumin in the synthesis of Acetonitrile /J.Chem. Soc. Japan, 1962, V.65. P 1360-1365.

10. Hammer R., Swann S. Synthesis of acetonitrile /Ind. Eng. Chem. 1949., 42., 2. 325 p.
11. Paushkin Ya.M., Osipova L.V. Properties, production and application of acetonitrile: // Uspekhi Chemii, 1959, Vol.28. Iss.3. P.237-264.
12. Zilberman E.N. Reaction of nitriles with hydrogen halides and nucleophilic reagents. // Uspekhi Chemii, 1962. V.31. No.12. P.1309-1348.
13. Boreskov G.K. Catalysts and catalytic processes. Novosibirsk, 1977. P.124.
14. Mukhlenov I.P. Technology of catalysts. L. 1988. P.19-31.
15. Yusupov D., Asadullaev M.A., Choriev R., Topilov R.S. Development and study of the properties of catalysts for the synthesis of acetonitrile // DAN RUz. 1999. No.8. P.38-39.
16. Choriev R., et all Research of the properties of heterogeneous catalysts of acetonitrile synthesis// PalArch's Journal of Archaeology of Egypt/Egyptology, №17 (6), (2020). – P.3225-3232.