Receipt of new catalysts used in the synthesis of acetaldehyde by separating the catalyst CCP into component parts

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Abstract. New catalysts have been developed and studied for the synthesis of acetaldehyde and acetone in combination with acetylene hydration. The composition of the feedstock CCP catalyst used in the acetaldehyde synthesis was analyzed and identified. Based on the analysis results, active cadmium oxide was separated from the CCP catalyst composition, and new BCC-1, BCC-2, BCC-3, BCC-4, BCC-5, BCC-6, BCC-7, BCC-8, BCC-9 catalysts were prepared. These catalysts were tested, and during the acetaldehyde synthesis process, the BCC-7 catalyst yielded a high efficiency (65.7%). Optimal conditions were determined for the synthesis of acetaldehyde and acetone. Bentonite mineral was used as a core in the preparation of this catalyst. There are different brands of bentonite mineral, and Bentonite (PBG) brand mineral was used for BCC-7 catalyst. The high content of aluminum oxide in this mineral increases the strength of the catalyst.

1 Introduction

Demand for acetaldehyde in the world is high, and acetaldehyde is considered a semi-finished product for the synthesis of acetic acid, ethanol, various pyridine derivatives, and others. Acetic aldehyde CH3CHO, compared to acetaldehyde, is colorless, transparent, highly flammable, and even boils at room temperature of 20 °C, easily soluble in water and organic solvents [1-3].

One of the most effective methods of obtaining acetaldehyde is by reacting acetylene with water in the presence of a catalyst (according to the Kucherov reaction). At "Navoiyazot" JSC, acetaldehyde is synthesized from methane homologs through acetylene hydration process using CCP (cadmium calcium phosphate) catalyst. It was found that due to the import of the catalyst into the currency account and the compatibility of the used catalyst with the output products, it is necessary to reprocess [4-6]. The length of this catalyst is 5-15 mm and its diameter is 3-5 mm, usually in a granular form or in tablet form with a graphite content of 1-1.5% by mass and a diameter of 4-5 mm. The average working time of the catalyst is 2500-3200 hours. Before using the CCP catalyst, it consists of 13% CdO [7-8].

Mechanism of Acetylene to Acetaldehyde Conversion Reaction

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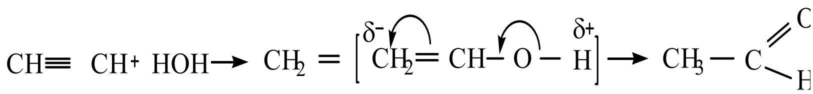
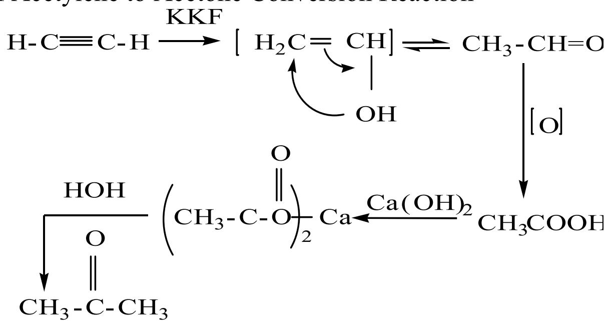
The Kucherov reaction is a chemical reaction that involves the hydration of acetylene homologs to produce carbonyl compounds. When acetylene is hydrated, acetaldehyde is formed:



The reaction was carried out in 1881 and was named the Kucherov reaction.

Mechanism of Acetylene to Acetone Conversion Reaction



2 Materials and methods

The research object is considered to be the acetylene substance being produced at Navoiyazot JSC. At Navoiyazot JSC, acetaldehyde is produced from the hydration of acetylene. The main catalyst of the chemical reaction is considered to be CCP (Cadmium Calcium Phosphate).

The following research methods were used to solve the tasks: physical-chemical analysis methods, analytical analysis method, and chromatographic method.

The object of research after the analysis is the substance acetaldehyde produced in Navoiazot Aj, and acetone and croton aldehyde, which is released as an additive.

Each chemical analysis method analyzed the results accurately.

This research paper presented the results of research on the synthesis of acetaldehyde using a heterogeneous catalytic method based on acetylene and water.

The most effective agent for the prepared catalysts was found to be the BCC-7 catalyst, which ensures an increased synthesis of acetaldehyde.

3 Results and discussion

In the analysis of the composition of the catalyst under the brand name CCP used, the following results were obtained (tab.1)

Table 1. Composition of CCP catalysts before and after use

Oxides in the composition of CCP **catalysts**	**Initial content of oxides in the composition of CCP catalysts (%)**	**Content of oxides in the composition of** CCP **catalysts after the experiment (%)**
CaO	47	46.43
CdO	13	10.63
P_2O_5	40	37.89
Additional substances	-	5.05

From the table, it can be seen that after using the catalyst and losing its strength, the content of CdO in the catalyst composition decreased from 13% to 10.63% (Table 1). Additionally, it is possible to observe that other catalysts may have been damaged by impurities.

In order to separate cadmium oxide from the used CCP catalyst composition, new catalysts (BCC-1, BCC-2, BCC-3, BCC-4, BCC-5, BCC-6, BCC-7, BCC-8, BCC-9) were prepared.

To separate the used CCP catalyst into its components, the catalyst was spread to a volume of 1 mm granules. 100g of spread CCP catalyst was dissolved in 1L of HNO_3 acid (1:1).

After dissolution, it was filtered. The mass of the filtered solution was 1185.5g, with a volume of 925ml. The remaining composition consisted of CaO-1.6%, CdO-0.1225%, P_2O_5-7.25%.

The solution was then purified from Ca (II) ions. Calcium ions were precipitated in sulfate form. For this, the initial solution was brought to a pH of 0 and 99g of Na_2SO_4 was added. After standing for a day, the mixture was filtered. The volume of the filtrate was 670ml, and the solid residue left on the filter paper, calcium oxide, weighed 219.5g, with a Ca content of 20.44% when analyzed. To completely precipitate cadmium oxide from the solution, it was neutralized with NaOH solution until reaching a pH of 7. Every minute, the pH was measured with litmus paper. When reaching pH 7, cadmium oxide precipitated and was left to settle for a day before filtering. The solid substance left on the filter paper, $Cd(OH)_2$, was washed with 1L of distilled water to remove nitrate ions and then dried for analysis. In this state, CdO accounted for 33.96% when analyzed. When analyzing the filtrate, it was found that CaO accounted for 0.775% and CdO for 1.519%.

In the process of reprocessing the CCP catalyst, the separated $Cd(OH)_2$ was treated with 1L of 1M H_2SO_4 solution. To further separate cadmium, the solution was passed through Purolite C-100 cation exchange resin. Initially, water was passed through the resin, and then the treated solution was passed through it.

The treated solution from the resin was analyzed. According to the results of the analysis, the resin retained all Cd within itself and the absence of Cd in the solution was confirmed. To completely separate Cd from the resin, a desorption process was carried out. For this purpose, 260ml of 2M HCl was slowly poured over the resin where Cd had been absorbed. The total volume of desorbed solution was 258ml, which was then analyzed. According to the analysis results, 1.82% CdO was present in the solution.

The obtained solution was used to prepare a catalyst. Bentonite mineral and active substance $Ca_3(PO_4)_2$ were used as additives. The solution was first boiled to improve its quality since it was necessary for all chloride ions to be removed from the solution.

Table 2. Mineral composition of various brands of bentonite

Bentonite mineral brands	Composition of compounds, %										
	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	MgO	CaO	Na_2O	K_2O	R_2O_5	q.m.	pH
Bentonite (PBG)	13.6	56.2	6.5	0.6	3.76	0.69	0.98	2.2	0.92	15.4	7
Bentonite (PPD)	8.7	46.8	-	-	2.74	10.1	-	1.6	1.99	24.3	8
Bentonite (PBV)	13.7	57.9	5.1	0.4	1.84	0.48	1.53	1.75	0.43	16.7	9.5

The method for preparing catalysts is described below:

Various catalysts were prepared by mixing bentonite and $Ca_3(PO_4)_2$ and analyzing the composition. The catalysts were first dried at room temperature and then in special drying ovens before being analyzed. According to the analysis results, various amounts of Cd oxide were found in the reprocessed catalyst composition with $Ca_3(PO_4)_2$ and bentonite mineral. The prepared catalysts had the following characteristics: they appeared as shiny tablets with a mass of 1.75 grams each. The diameter was 0.5 mm, and the length was 1.25 mm.

X-ray diffraction analysis of the sample (Figure 1).

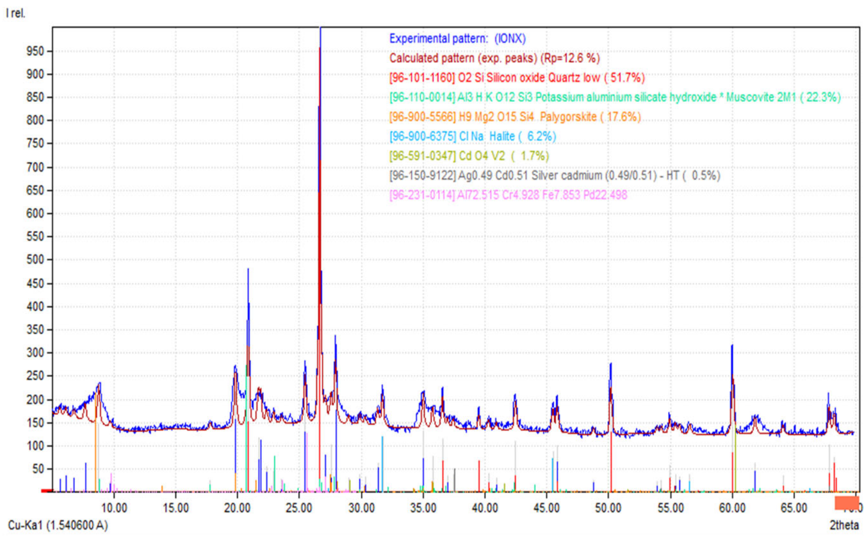


Fig. 1. The initial catalyst sample mass consisted of 51.7% silicon oxide, 2.2% cadmium oxide, 22.3% aluminum silicate, 17.6% magnesium oxide, 6.2% sodium chloride, etc. It was found that the yield of the final product increases significantly with an increase in the amount of cadmium oxide in the catalyst.

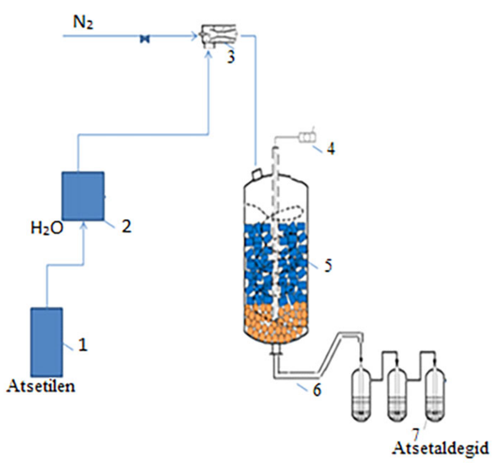


Fig. 2. Experimental setup for the synthesis of acetaldehyde from acetylene hydration in a catalytic manner. 1- acetaldehyde flask, 2- water, 3- nitrogen gas line injector, 4- temperature gauge, 5- reactor, 6- cooler, 7- gas collector.

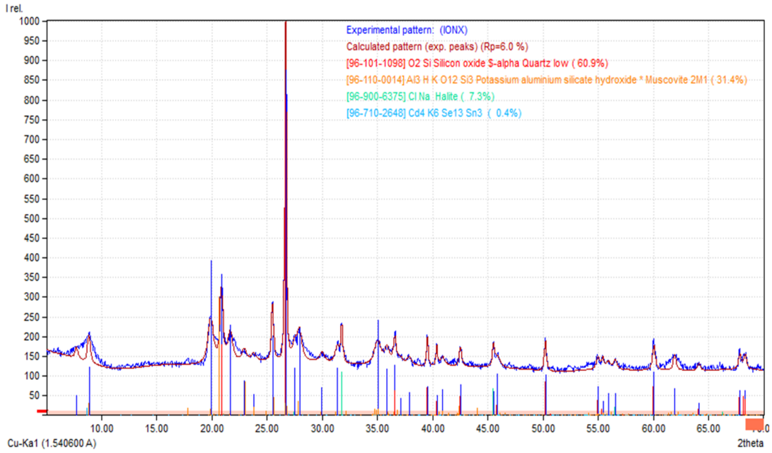


Fig. 3. The mass of the catalyst sample after the test consists of 60.9% silicon oxide, 0.4% cadmium oxide, 31.4% aluminum silicate, 7.3% sodium chloride, etc. It was found that the amount of cadmium oxide in the catalyst was significantly reduced.

Table 3 The catalysts with different compositions were used for the synthesis of acetaldehyde from acetylene through catalytic methods.

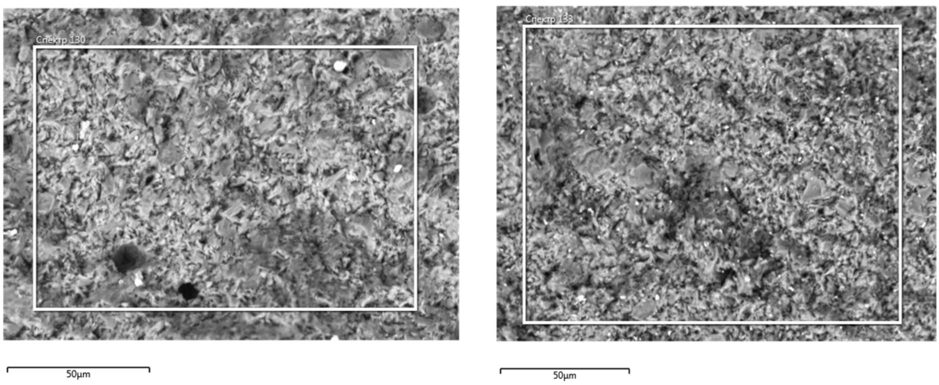
№	**Catalyst name**	**Catalyst composition, %**	**Temperature, °C**	**Catalysis time**	**Products obtained**			
					Acetaldehyde %	**Acetone %**	**Crotonaldehyde**	**Additional substances**
1	BCC-1	60- Bentonite 10-CdO 30-$Ca_3(PO_4)_2$	100-150	62	45.5	28.7	14.2	11.6
2	BCC-2	70- Bentonite 10-CdO 20-$Ca_3(PO_4)_2$	100-150	72	50.7	39.04	6.9	3.38
3	BCC-3	80- Bentonite 10-CdO 10-$Ca_3(PO_4)_2$	100-150	62	42.6	26.6	17.4	9.4
4	BCC-4	60- Bentonite 15-CdO 25-$Ca_3(PO_4)_2$	100-150	72	53.7	32.6	10.6	3.1
5	BCC-5	70- Bentonite 15-CdO 15-$Ca_3(PO_4)_2$	100-150	82	55.9	38.06	4.5	1.54
6	BCC-6	80- Bentonite 15-CdO 5-$Ca_3(PO_4)_2$	100-150	62	47.9	24.5	15.2	12.4
7	BCC-7	60- Bentonite 17-CdO 23-$Ca_3(PO_4)_2$	100-150	92	65.7	27.4	4.9	2
8	BCC-8	70- Bentonite 17-CdO 13-$Ca_3(PO_4)_2$	100-150	82	52.3	36.03	8.06	3.61
9	BCC-9	80- Bentonite 17-CdO 3-$Ca_3(PO_4)_2$	100-150	72	49.3	26.07	16.5	8.13

The optimal conditions for the production of acetaldehyde and acetone were determined, and the results are presented in the following table.

Effect of concentration of catalysts on yield of acetaldehyde formation

The effect of catalyst concentration on the production of acetaldehyde was analyzed based on the table above (Table 3), showing that when using the BCC-7 catalyst, the acetaldehyde content reached 65.7%. It can be seen that the BCC-7 catalyst had a higher efficiency compared to the remaining catalysts.

Furthermore, scanning electron microscopy images were obtained before and after the use of the prepared BCC-7 catalyst in the process of acetaldehyde synthesis.



a b

Fig. 4 Images of a catalyst prepared under the BCC-7 brand with a size of 50 micrometers (µm): a-before folding; b-after folding.

4 Conclusion

The obtained CCP catalyst was analyzed and active cadmium oxide was separated from the CCP catalyst composition, resulting in the preparation of new BCC-1, BCC-2, BCC-3, BCC-4, BCC-5, BCC-6, BCC-7, BCC-8, BCC-9 catalysts.

These catalysts were used, and during the acetaldehyde synthesis process, the BCC-7 catalyst yielded a high efficiency (65.7%). Optimal conditions for the synthesis of acetaldehyde and acetone were determined. Bentonite mineral was used as a core in the preparation of this catalyst. There are different brands of bentonite mineral, and Bentonite (PBG) brand mineral was used for BCC-7 catalyst. The high content of aluminum oxide in this mineral increases the strength of the catalyst.

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