

Production of Cadmium-Calcium-Phosphate Catalyst of Acetaldehyde Synthesis

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ABSTRACT

The technology of production of acetaldehyde at JSC "NAVOIYAZOT" (Uzbekistan) supposes an application of "Cadmium-Calcium-Phosphate catalyst (KKF-C)" made according to TU 113-03-00209510-108-2006, developed by NIAP (Novomoskovsk city, Russia). It was proposed to engage into its recycling the wastes of KKF-C.

Keywords: Production Of Acetaldehyde, Catalyst, Cadmium-Calcium-Phosphate Mass; Catalytic Activity Test.

INTRODUCTION

Acetaldehyde is produced by passing an acetylene-vapor mixture through a bed of catalyst at a temperature of 340-350 °C and a pressure of 0.2-5-0.7 atm. This production exists in JSC "NAVOIYAZOT" (Uzbekistan). The "Cadmium-Calcium-Phosphate catalyst (CCP-C)" is used according to TU standard 113-03-00209510-108-2006, developed by NIAP (Novomoskovsk, Russia).

The term of its service is not long: it takes a reboot every 3-6 months, for which a new CCP is purchased. Meanwhile, it is possible to process the spent catalyst and return the extracted components to a new cycle of synthesis of the CCP. In the Uzbekistan republic, no studies have been carried out yet to develop a technology for the synthesis of the catalyst for the CCP.

Although the raw material for its synthesis is available in Almalyk GMK JSC, as well as in the form of a spent catalyst, the CCP, but the methods of its preparation are not covered in the literature, there are no data on modes and description of technological equipment.

To establish own production of the CCP, it is necessary to develop an appropriate technology.

There is a long-standing interest in calcium phosphate, a catalyst for the acetylene hydration process [1], but only in combination with components (calcium). The role of phosphate in

such a composition revealed the need for basic phosphates [2]. In the sediment of the CCP [5,11] mass, its aging takes place [6], the solution contains an excess of NO₃⁻ ions; HOP₄²⁻, interacting with CaHPO₄ [5-7].

From the patent literature, a method of using a CCP catalyst at a temperature of up to 380 °C and a pressure of 0.2-0.7 atm is known [3]. Another method provides the preparation of the CCP catalyst from nitrates, by decomposition of apatite concentrate with nitric acid [4]. The preparation of the raw material component - cadmium hydroxide is well studied [8].

The purpose of the work: a reasonable choice of ways to synthesize the catalyst CCP, the production of CCP samples, the study of their properties and transfer to a laboratory pilot-industrial test at JSC "Navoiyazot" (Navoi city, Uzbekistan), the development of a technological map for industrial synthesis of the catalyst CCP from local raw materials.

METHODS AND MATERIALS

The mass fraction of cadmium oxide (CdO) [8] is determined according to TU standard 113-03-00209510-108-2006. For the synthesis of CCP, a method of precipitating a catalyst mass from hydroxides, cadmium salts, calcium in the presence of a calculated amount of phosphate ions was used [9].

The composition of the product was studied. The precipitation of the mass was carried out by

adjusting the pH of the medium, T°C. The optimal pH range (6.8-7.1) is selected, which is associated with hardware limitations. The laboratory thermostat, pH meter EV-74 was applied.

RESULTS AND DISCUSSION

In the spent catalyst CCP, on storage in the shop of JSC "Navoiyazot" there are 82 tons of material, its composition is the following: CaO - 43.85%; CdO = 11.40; P₂O₅ - 33.21 with the ratio (CdO + CaO)/(P₂O₅) = 3.78 (1). It must be replaced with a newly synthesized product.

A method has been developed for synthesizing the catalyst mass of a CCP, consisting in draining a mixture of solutions in the required molar ratio: Ca(NO₃)₂ + Cd(NO₃)₂ and (NH₄)₃PO₄. Precipitation is carried out in a fume hood, in an apparatus from a container, with a stirrer for suspension and separating funnels [10-11].

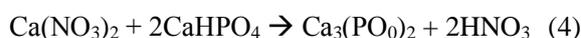
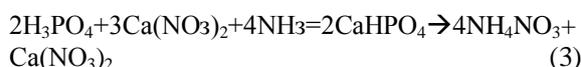
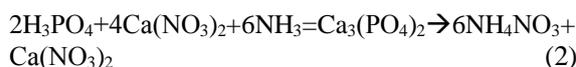
The deposition time is 90 min, the temperature (20+25 °C), pH 6.8-7.0. Under these conditions, the desired structure of the sediment is formed, its ability to filter and wash.

Monitoring of the pH of the medium was carried out by manual pulp sampling from the middle part of the precipitator and measurement on an EV-74 pH-ionomer every 30-60 sec.

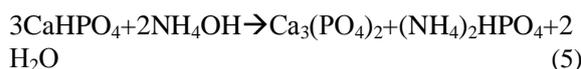
Maintaining pH values of 6.8-7.1 is associated with the effect on them of the discharge rate of reagent solutions, their mass ratio, side and parallel reactions in the mixer, associated with the chemical aging of the suspension, the chemical composition of the precipitate and the mother liquor. Initially, a precipitate of CaHPO₄·2H₂O and a solution containing an excess of NO₃⁻ ions are found in the resulting system; HOP₄²⁻, interacting with CaHPO₄ in the sediment. As a result, the process of the (top chemical) transition of CaHPO₄ to the more basic Ca₅(PO₄)₃OH salt and its reverse transition to CaHPO₄ is established, in the presence of nitric phosphoric acids. In addition, the structure of the precipitate depends on the duration of the

precipitation. The optimum time of formation of the desired precipitate: (1.5-2.0) h.

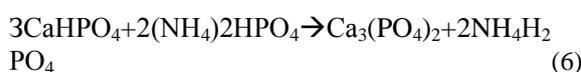
The process is described by the equations:



The local and total excess NH₄OH shifts the equilibrium to the right:



With an excess in the pulp of the HPO₄²⁻ ions, conditions are created for the reaction:



Optimal synthesis conditions were selected: separate drainage of solutions (NH₄)₃PO₄ and a mixture of Ca(NO₃)₂ + Cd(NO₃)₂ into the precipitant, with stirring, pH 6.8-7.1 pulps.

Precipitation was carried out at the ratio of the reagents Ca(NO₃)₂ + Cd(NO₃)₂ and ammonization of phosphoric acid to pH (8.0-9.4) [10]. Deposition time is 90 min. Samples of the catalyst mass of the CCP corresponded to TU standard 113-03-5761673-43-92 in chemical composition at pH (6,8-7,1) (Table 1).

If this interval of pH was not observed, the content of the mass fraction of P₂O₅ varied from 43% to 59%; CaO from 34% to 55%; CdO - from 5.5% to 13%. The molar ratio (1) was 2.0+2.8. Precipitation obtained at a pH greater than 7.1 had a low filtration rate. At pH less than 6.8, the precipitates were enriched with P₂O₅ (more than 52% by weight).

Most of the samples were obtained by precipitation of calcium nitrates, cadmium with an excess of ammonium phosphate. Excess phosphate remained in the filtrate, which resulted in non-reproducibility of the samples by chemical composition.

Table 1. Effect of pH of the medium on the parameters of the product of CCP (pH adjusted with additives NH₄OH or (NH₄)₃PO₄).

pH of the medium	Content, % mass			<u>CdO + CaO</u> P ₂ O ₅	Conformity to TU standard 113-03-00209510-108-2006
	CdO	CaO	P ₂ O ₅		
6.8-7.1	11.5±1.5	42.5±2.5	45.0±2.0	2.65-2.90	Corresponds to the norm
> 7.1	< 11.5	< 42.5	< 44	2.95	Does not match
< 6.8	< 9.5	< 40	> 52	2.20	Does not match

Table 2. Physical and mechanical properties of the catalyst CCP

No.	Name of indicator	Technical characteristics
1	Bulk density, kg/dm ³	0.9±0.1
2	Mechanical strength, kg/cm ² - abrasion, %, not more than - for crushing, %, not less than	12.0 90.0

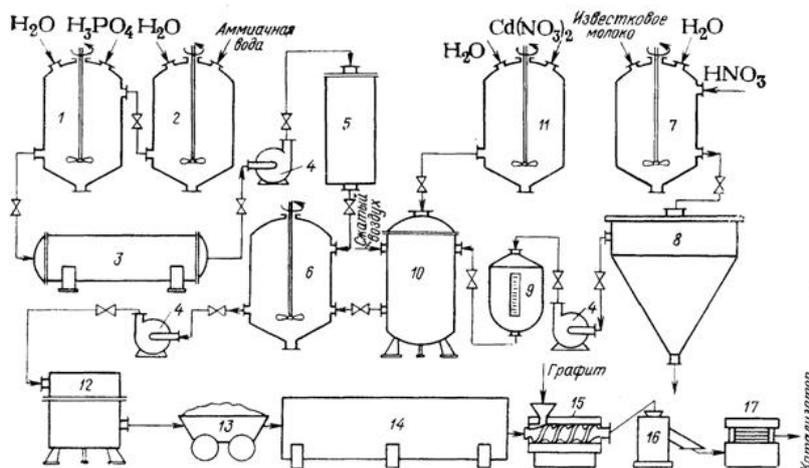


Fig 1. The scheme of production of cadmium-calcium-phosphate contact mass: 1 - tank reactor; 2 - a spray tank; 3 - the filter; 4 - the pump; 5 - collection reactor; 6 - precipitating tank with a stirrer; 7 - tank-reactor with a stirrer; 8 - sedimentation tank; 9 - measuring point; 10 - collection; 11 - solvent tank with a stirrer; 12 - automatic filter press; 13 - a trolley; 15 - a mixer of a firm phase; 16 - agitator; 17 - tablet agitator.

The ratio of phosphates formed in the pulp depends on how well the liquid phase is mixing and at what levels the solutions are fed into the reactor.

Of no less importance is the sealing of the tanks in which precipitation occurs. In an open vessel, three calcium phosphate forms slowly.

Phosphates in the samples are present in the form of acid salts (dicalcium- and dicadmium-phosphates).

A technological scheme for obtaining the PCF was developed, consisting of the steps:

- Preparation of a solution of ammonium phosphate at a temperature of <math> < 35 \text{ }^\circ\text{C}</math>:

$$3\text{NH}_4\text{OH} + \text{H}_3\text{PO}_4 \rightarrow (\text{NH}_4)_3\text{PO}_4 + 3\text{H}_2\text{O} \quad (7)$$
- Preparation of a solution of calcium and cadmium nitrates

$$\text{Ca}(\text{OH})_2 + 2\text{HNO}_3 \rightarrow \text{Ca}(\text{NO}_3)_2 + 2\text{H}_2\text{O} \quad (8)$$

$\text{Cd}(\text{NO}_3)_2$ - as a dry salt is dissolved in water and mixed with the settled solution of $\text{Ca}(\text{NO}_3)_2$.
- Precipitation of Ca, Cd phosphates is carried out with constant stirring and simultaneous feeding at different levels in the solution precipitator:

$$\text{Ca}(\text{NO}_3)_2 + \text{Cd}(\text{NO}_3)_2 \text{ and } (\text{NH}_4)_3\text{PO}_4 \text{ for } 1.5\text{-}2 \text{ hours at a temperature of } 20\text{-}25 \text{ }^\circ\text{C, pH } 6.8\text{-}7.1.$$

- Filtering the suspension and washing the precipitate from NO_3^- ions.
- Drying, precipitation at a temperature of 100-110 °C and tableting.

Catalyst CCP, produced by this technology, is characterized by high activity, selectivity of action and stability (2600 hours of operation). It is a tablet of a cylindrical form of light gray color, not combustible, not explosive. According to its physical and mechanical properties, it meets the requirements of Table 2.

The technical name of the product is a cadmium-calcium-phosphate catalyst (CCP-C) for the vapor-phase hydration of acetylene to acetaldehyde at a temperature of 340-380 °C, a pressure of 0.2-0.7 kgf/cm² and a vapor-gas ratio (V:G) in the reaction zone of the vapor catalyst bed (10:14). It could be used in the production of acetic acid, butadiene, acetal-zole, pentaerythrite, aldehyde type synthetic resins.

A scheme for the production of the CCP is proposed (Fig. 1).

CONCLUSION

A technological scheme for the preparation of a catalyst for the synthesis of acetaldehyde from an acetylene-vapor mixture was developed in the laboratory. The samples of the catalyst CCP were obtained at the following parameters:

concentration: $\text{Cd}(\text{NO}_3)_2$ solution, in terms of CdO , 22.8 g/dm^3 ; solution of $\text{Ca}(\text{NO}_3)_2$, in terms of CaO , 103.6 g/dm^3 ; solution of orthophosphoric acid - 25% by weight. The concentration of ammonia water is 10% by weight. Precipitation of the CCP mass was carried out at pH 6.8-7.1; within 90 minutes; filtration and washing of the sediment - until the absence of NO_3^- ions; drying - at a temperature of 100-110 °C to constant weight; then crushing, mixing with graphite (2% by weight) and tableting. A technological process map has been created, the operating mode is periodic; developer is Institute of general and inorganic chemistry of Uzbekistan Academy of sciences. The characteristics of the product and the description of the technological scheme are offered. A 1 kg batch of CCP catalyst was produced and transferred to JSC "Navoiazot" for activity testing.

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