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Catalytic Vapor Phase Hydration Acetylene and Its Derivatives

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Abstract

The reactions of the synthesis of acetylene from direct hydration of acetone on catalysts prepared from oxides and fluorides of zinc, cadmium, iron, chromium and aluminum. The basic texture and performance characteristics of the synthesized catalysts were studied. . According to the experimental data producing acetaldehyde, acetone from the catalytic hydration of acetylene is proposed.

Keywords: acetylene, acetone, hydration, nanocatalyst, kinetics and mechanism, technological scheme.

Introduction

The vapor phase hydration of acetylene to form acetone on the multifunctional catalysts has been studied. The parameters of the process to ensure the production of acetone with high selectivity and conversion of acetylene were investigated. Currently acetaldehyde is mainly prepared by two methods – acetylene hydration and ethylene oxidation [1,2].

The sol-gel process is one way to obtain nanocatalysts based on the synthesis of inorganic colloidal particles and inorganic-organic hybrid materials. Application of sol-gel method can provide crystalline nanoparticles and lower the temperature of the single-phase synthesis of the product which makes them usable in petroleum chemistry. Therefore, at present it is a very urgent studies on the synthesis of nanocatalysts for petrochemical synthesis. Synthesis was carried out by nanocatalyst gel deposition from aqueous solutions of the precursor components followed by high-temperature treatment of the resulting precipitate.

As a result of experiments conducted to select an effective catalyst having high activity, selectivity, and stability performance actions. Designed catalyst for a long time retains its activity. The influence of temperature, water ratio: acetylene, volume rate, the catalyst composition on the yield of the desired products and the degree of conversion of acetylene.

The hydration process of acetylene to acetic aldehyde in the presence of catalysts studied reasonably well. For this process, numerous catalysts proposed [3-5]. Among known catalyst hydration of acetylene to the acetic aldehyde cadmium-calcium-phosphate proved the most active catalyst (FCC), which is recommended for industrial application [6]. However, cadmium-calcium-phosphate catalyst is not without drawbacks. Average yield acetaldehyde per cycle acetylene does not exceed 7.0%. FCC catalyst is very sensitive to changes in temperature, its life before regeneration is not more than 72-76 hours.

Hydration of the acetylene in the presence of catalyst may be carried out to obtain acetone. The advantage of this method is feasibility of the process in existing production of acetaldehyde. Altering cadmium-calcium-phosphate to zinc-containing catalyst provides a catalyst acetone in good yield with little change in technology [7].

Experimental

The hydration reaction of acetylene to acetaldehyde performed under flow conditions in a stainless steel reactor size dxh = 25xl000 mm, 50,100,150,200 cm^3 bulk catalyst volume. Assays were performed on GLC chromatography LHM 8-MD (NF-Apiezon-M/zeolite-545, detection is thermal conductivity, the helium gas flow rate was 60 cm^3/min, column temperature 80°C).

Surface area, crush strength, total pore volume and the ash content of the samples were determined. The specific surface area was determined by thermal desorption in a flow of nitrogen gas carrier - helium at liquid nitrogen temperature, treating the experimental data on the BET equation.

The mechanical strength of the granules on crash measured on a "Strong measures PC-1", for testing of granular materials in mechanical strength under compression statistical method. For the analysis

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result the arithmetic mean value of individual 25 tests. The total pore volume of the pellets was calculated by the formula

$$V = \frac{1}{p_k} - \frac{1}{p_p}$$

where p_k, p_p - and the apparent and pycnometric density of granules g /ml, respectively.

The apparent density of the pellets was determined measuring their volume excluding internal pores. The amount of pellets found by immersing them in a solid powder (quartz sand with a particle size of 0.063-0.1 mm).

Results and discussion

We have studied the process of catalytic vapor phase hydration of acetylene and its derivatives in the presence of complex mixed multifunctional catalysts. During the production of acetaldehyde as a catalyst was used cadmium fluoride on alumina promoted with aluminum fluoride. In the synthesis of acetone as the catalyst was used zinc oxide supported on alumina, promoted with cadmium fluoride and aluminum the following compositions , % by weight: ZnO-20.0-25.0; CoF_2-3.0-5.0; $A1F_3$-3.0-5.0; Al_2O_3-60.0-84.0.

The composition and properties of the synthesized catalysts for the synthesis of acetaldehyde and acetone are shown in Table 1.

Table 1

The composition and properties of the synthesized catalysts.

№	Contents, mass %	Relative notation	Surface activity, m^2/g	Hours before regeneration	Total product yield, %	
					CH_3CHO	Acetone
1	ZnO-20.0 AlF_3 – 3.0 Al_2O_3 -77.0	SXA-1	135,0	72,0	10,0	82,0
2	CdF_2 – 20.0 Al_2O_3 – 80.0	KA-1	186,0	96,0	75,0	5,0
3	CdF_2 -18.0 AlF_3 -3.0 Al_2O_3 – 79.0	KA-2	210,0	96,0	82,0	3,0
4	CdF_2-18.0 AlF_3-2.0 Cr_2O_3-5.0 Al_2O_3 -75.0	KXA-1	225,0	120,0	83,0	1,5
5	ZnO-18.0 CdF_2-2.0 Cr_2O_3-5.0 Al_2O_3-80.0	UKXA-1	165,0	120,0	3,0	86,0

The hydration reaction of acetylene to acetaldehyde conducted in the presence of cadmium-chromium-aluminum - KXA catalyst in the temperature range 360-460°C.

The effect of the ratio of acetylene: water on the selectivity of acetaldehyde interval acetylene: water = 1: 1-10 mol. Thus established that acetylene ratio range: -water = 1: 1-1: 3, an increase share auxilary products. Out of acetaldehyde not exceeded 26.0% on reacted acetylene. When ratio-1: 4-1: 6 conversion output of acetaldehyde and acetylene peaks. A further increase in the ratio of acetylene water gives practically no effect.

It was established experimentally that the yield of acetaldehyde and acetylene conversion significantly

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depends on the space velocity of acetylene.

Effect of volume rate on acetylene yield to acetaldehyde and its conversion studied WHSV ranging from 50 to 120 hours (Figure 1).

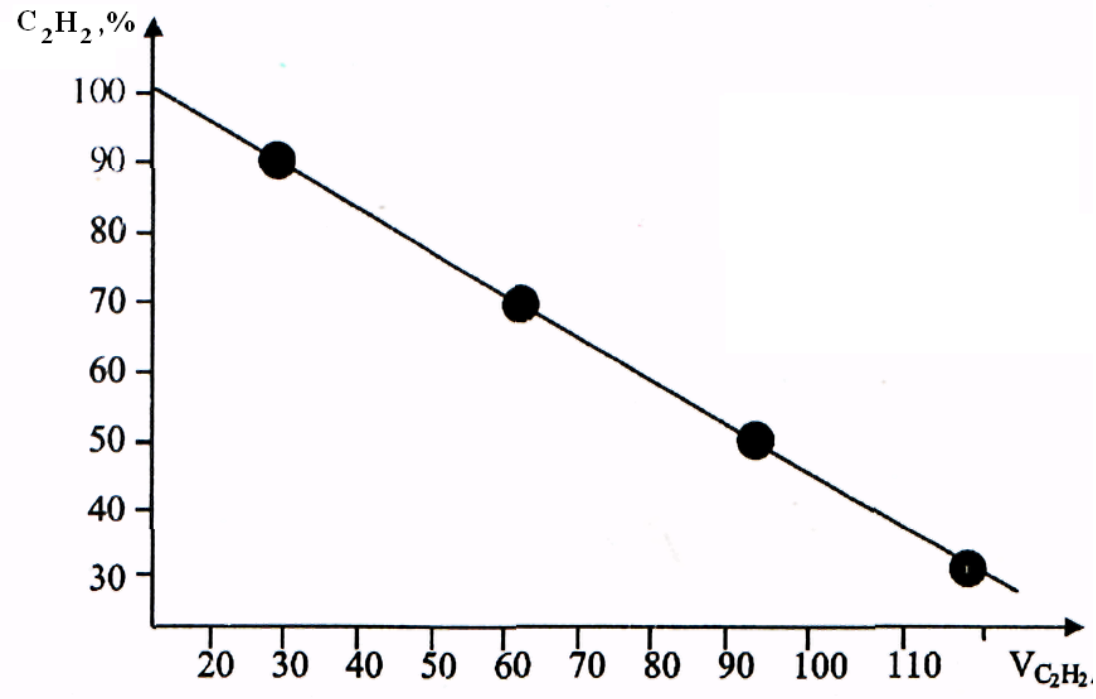

Fig.1. Effect of space velocity on its acetylene conversion.

The effect of temperature, the grain size of the catalyst reactor parameters, the height of the catalyst bed in the process parameters were studied. It is found that the reaction of acetaldehyde synthesis starts with 350°C. In order to maintain conversion acetylene at 70-75% of the reactor temperature was raised to 10°C every 10 hours. It is found that the optimum height ration catalyst bed reactor diameter equal to 50-60 WHSV acetylene -50-60 hour. In these circumstances, KXA-1 rolled-jam with constant activity works up to 120 hours and the regeneration within 16-24 hours completely restores its activity.

Substitution on cadmium-chromium-aluminum catalyst to zinc-alumofluoride or zinc-cadmium-chromium-aluminum catalyst leads to the formation of acetone as the major product during the hydration of acetylene.

In order to establish the technological process parameters of producing acetone by the direct hydration of acetylene we investigated the effect of space velocity, temperature, the ratio of acetylene: water, and other output of acetone,

The influence of temperature was studied in the range of 250-500 (Table 2).

Table 2.

Effect of temperature on the conversion of acetylene

Temperature, 0°C	Yield acetone on reacted acetylene %	Acetylene conversion,%
250	15,2	18,0
300	20,6	26,0
325	33,4	34,0
350	63,0	62,0
375	70,6	80,0
400	82,0	84,0
425	84,0	90,0
450	65,0	94,0
500	52,0	98,0

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In the presence of 1-SKA catalyst at a ratio of acetylene water = 1: 4 molar acetylene at a flow rate of 80 hour^{1}.
As seen from the table, 1-SKA catalyst is ineffective to 350°C. From 350°C to 425 ° C, there is a smooth increase in the conversion yield of acetone and acetylene. Further increase in temperatures leads to a significant decrease in the yield of acetone by percolation byproducts.
In order to confirm the above, we performed thermodynamic calculation of gross - the process of formation of acetone.

$$2C_2H_2 + 3H_2O \rightarrow CH_3 - CO - CH_3 + CO_2 + 2H_2$$

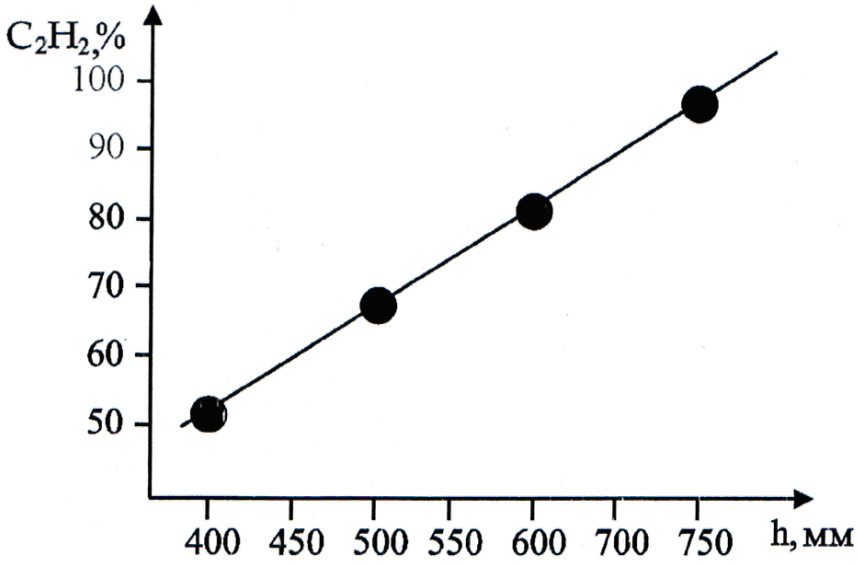
At the same time found the following value
$\Delta H^0_{298}, \Delta S^0_{298}, \Delta G^0_{298}$

$\Delta H^0_{298} = -334{,}4 \text{kJ/mol}$

$\Delta S^0_{298} = -121{,}2 \text{ kJ/mol.grad}$

$\Delta G^0_{298} = -367{,}5 \text{ kJ/mol}$

These data show that the formation of acetone in a wide range irreversible temperature and proceeds exothermically.
The dependence of the Gibbs energy change of temperature. It was found that the Gibbs energy decreases from - 87,917 cal/mol to - 100,967 kcal/mol in the temperature range of 298°K to 723°K.
The influence of the height of the catalyst bed to change the degree of conversion of acetylene (Figure 2).



As seen from the figure with the increasing height of the catalyst layer increases the degree of conversion of acetylene, which confirms process flow in the inner diffusion region.
In the production of acetylene by pyrolysis of natural gas forms as a byproduct. Allen methylacetylene fraction the amount of which is 76.90 kg/h with a unit capacity of 5 t/h. Methylacetylene-allene fraction has not yet been found application and burned.
We investigated the hydration process methylacetylene-allene fractions in the presence SKA-1 catalyst in the temperature range 350-450°C. It is found that by passing the methylacetylene-allene fractions ratio water in 1: 2 as the major product formed acetone by the scheme:

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$$CH_2 = C = CH_2 \rightarrow CH_3 - C \equiv CH \xrightarrow{HOH} CH_3 - C(OH) = CH_2 \rightarrow CH_3 - CO - CH_3$$

The effect of temperature, volume rate, the ratio of methyl acetylene-allnovaya fraction Water etal. the output of acetone. When op¬timalnyh conditions obtained acetone to yield 86.0% at a conversion of methyl acetylene-allene fraction 92,0-94,0%. Based on the results it has been improved existing technology acetylene hydration on public corporation “NAVOIYAZOT”. Scheme of technology producing acetaldehyde, acetone (or mixtures thereof) is shown in Fig.1.

According to the arrangement, the heat exchanger via pump metered water and heated to a temperature of 80-850°C. The heat exchanger 3 is fed from a gas tank 2 acetylene pressure 0.12-0.15 MPa. Saturated steam of acetylene gas mixture enters the top of the reactor where the catalyst is heated to the temperature 360°C. (Reactor - basketry, multichamber). The reaction is exothermic. Acetaldehyde, acetone and other reaction products are separated from the gas stream by washing with water. Steam-gas mixture enters the reactor to the heat exchanger 5, where a portion condenses catalyst output. Uncondensed part comes into the column 7 on the absorption of water. The condensed portion of catalyst output exchanger column and collected in the tank 6 and then sent to distillation. The distillation column is first isolated acetaldehyde, then acetone. The bottom residue consisting of croton aldehyde, paraldehyde, water and others are forwarded for processing. Unreacted part acetylene (average 20%) in a mixture with hydrogen and carbon dioxide after the column is directed to recycling.

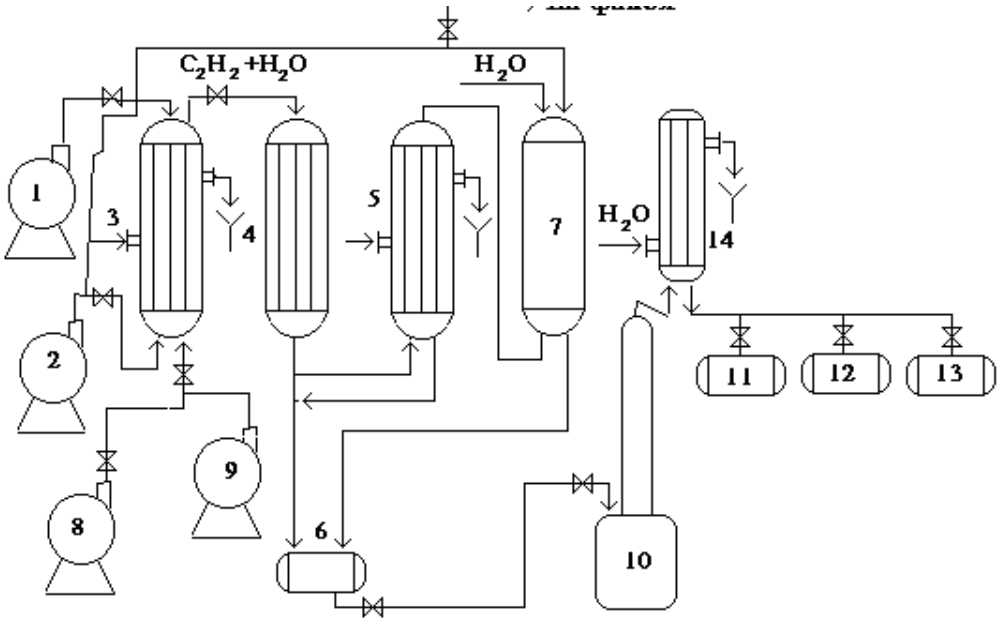

Fig.1. Technological scheme of the hydration of acetylene.
1 pump; 2 acetylene gas tank; 3 heat exchanger; 4 reactor; 5 exchanger; 6 tank catalyst output; 7 absorption column; 8 blower; 9 nitrogen gas tank; 10 stage distillation column; 11 tank acetaldehyde; 12 tank acetone; 13 tank bottoms; 14 exchanger.

Conclusions

1. Study of the direct synthesis reaction of acetone to acetylene hydration catalysts prepared from oxides and fluorides of zinc, cadmium, iron, chromium and aluminum with a peptizing agent in a solution of acetic acid accomplished. The basic texture and performance characteristics of the synthesized catalysts is determined.
2. Based on the study of the degree of conversion, the stability of the catalyst and the yield ratio of water: acetylene found that catalyst №5 stably operated for 125-144 hours (assuming the temperature rise at 10°C after 20 hours), providing a degree of acetylene conversion at 91-95% and the yield of acetone - 90-92%.
3. A technological scheme of acetaldehyde, acetone catalytic hydration of acetylene is proposed.

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