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Modernization of the Catalyst Composition for the Synthesis of Acrylic Acid Nitrile in Aqueous and Non-Aqueous Media

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ABSTRACT

The effect of the components of the catalyst solution for the hydrocyanation of acetylene on the activity and selectivity of the process under liquid-phase conditions has been studied.

The introduction of $ZnSO_4$ and ZnO additives into the shop catalyst did not give a positive effect under these conditions.

Studies of catalysts in non-aqueous media lead to an increase in their activity and selectivity in comparison with aqueous media. It has been shown that the composition of the CuCl - NMP - DMF catalyst is characterized by high activity (up to 32 g / l.h.) and selectivity (83-90%), i.e. the activity of this composition is almost twice as high as compared to the water-based ones (12-18 g l.h.).

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In order to increase the productivity of the catalyst for the production of acrylic acid nitrile (NAC), together with the central laboratory association (CLO) "Navoiazot" (Republic of Uzbekistan), studies of the synthesis of NAC by hydrocyanation of acetylene were carried out in a laboratory unit in the presence of liquid-phase catalysts. And also p / o "Navoiazot" have developed [1,2] a new, more efficient catalyst composition for the synthesis of vinyl acetate based on acetylene.

In the operating shop of the NJSC p \ o "Navoiazot", the liquid-phase (water) hydrocyanation of acetylene with the formation of acrylonitrile is carried out on a shop catalyst of the following composition \% mass \ CuCl-30; NH_4 CI-15; H_2 O-52. This catalyst composition has a number of disadvantages: low productivity of 12-15 g per liter of catalyst per hour, therefore, low catalyst activity and insufficient rate of acetylene dissolution, as well as a short service life [3,4]. The mechanisms of the process of synthesis of NAC hydrocyanation of acetylene are indicated in the literature [3,5].

One of the more economically viable ways to intensify the process of NAC synthesis is the use of various activating additives to the existing shop-floor catalyst. The process can be carried out in a non-aqueous aprotic solvent without additives or in the presence of various additives. The developments of these processes were investigated in this work.

The following types of catalysts have been tested in a laboratory facility;

1. Water-phase shop catalyst with or without additions of $ZnSO_4$ and ZnO.
2. CuCl catalyst in a mixture of non-aqueous solvents;
   A) dimethylformamide (DMF) without additives.
   C) with additives such as AgCl, CCl_3 COOH, concentrated HCl and AgCl with phosphoric acid.

The catalyst with the addition of ZnO was tested in the same way. Due to the poor solubility of the additives in the catalyst solution, experiments with other concentrations were not performed. The results of the experiments are presented in table No. 1. The table contains the average data of the separate periods with a stable regime and the highest NAC output.

Tests in aqueous solution were carried out in the following mode

Acetelene consumption is 30 l / hour. "Breakthrough" HCN 0.2-0.5% vol. Temperature in the reactor 85 $_-^+$ 3 ^{0}C

The consumption of hydrocyanic acid was calculated based on the amount of HCN consumed for a certain time.

Analysis of the work of the shop catalyst with additives												Table no. 1	
No.	Catalystcomposition	Continue slave. cat hour	Consumption		Reactiongascomposition								
			C_2H_2 l / h	HCN l / h	HAK	HCN	Bx	BA	AA	Xp			
1.1.	Originalshopfloor	4	32.5	3.6	II, 07	0.30	0.31	0.9I	3.58	0.06	14.82	69.49	92.86
		thirteen	32.3	2.0	10.03	0.23	0.45	0.89	3.60	0, I2	13.43	66.46	91.43
		29	34.2	2, I	9.25	0.33	0.35	0.47	3.04	0.07	12.39	70.18	98,00
ZnOadditive													
1.2.	With the addition of ZпO	3	32.6	3.6	9.65	0.40	0.28	I, 63	4.08	0.08	I2.92	6I, 39	94.28
		15	35,7	3.6	10,00	0.26	0.46	I, I0	3.47	0.13	I3.39	65.96	102.28
		23	33.4	3.6	9.66	0.51	0.53	0.65	2.57	0.08	I2.24	71.61	95.43
		39	7	2.0	9.80	0.54	0.48	0.57	3, I9	0.07	I2.53	69.40	96.20
2.1.	Originalshopfloor	9	33.5	4.0	7.72	0.36	0.25	1.23	1.99	0.02	15.66	68.87	96.00
		eighteen	34.5	3.6	8.95	0.42	0.26	1.15	2.25	0.06	18.15	70.64	97.54
		21	32.0	3.0	9.05	0.44	0.27	1.11	2.05	0.04	18.35	72.28	92.14
Additive $ZpSO_4$													
2.2.	Withadditive $Zп SO_4$	5	31.0	2.8	7.08	0.37	0.27	0.96	2.57	0.06	14.36	64.72	88.57
		14	30.5	2.8	7.51	0.42	0.28	0.96	2.53	0.08	15.23	66.11	87.63
		25	31.0	2.1	7.18	0.40	0.28	0.85	2.06	0.05	14.56	68.91	88.57

Analysis of the shop catalyst with additions of $ZnSO_4$ and ZnO was performed in comparison with the original shop catalyst. (Table 1) For this, preliminary synthesis of NAC in a laboratory unit was carried out on a shop catalyst, and the next synthesis on the same shop catalyst with the addition of $ZnSO_4$ in an amount of 4.0%. When a shop catalyst with $ZnSO_4$ and ZnO additives was used, the selectivity of the catalyst in comparison with the shop catalyst almost did not change, the activity even decreased, and there was no visible change in other indicators either.

The reasons for the low productivity of the catalyst composition, as well as the various by-products, are due to the use of water as a medium, since acetylene is slightly soluble in water. In order to improve the productivity of the process and reduce undesirable by-products, we used a dipolar aprotic solvent, dimethylformamide (DMF), as a solvent. DMF is one of the best solvents for acetylene; therefore, it was assumed that the activity and selectivity of the catalyst composition would improve in this environment.

Analysis of the operation of a non-aqueous catalyst for the synthesis of NAC Table no. 2

No.	Composition catalyst	Continue slave. cathour	Temperature	Consumption		Reactiongascomposition						Activate g / l. Hour	Selek-th%	Volumetric Speed
				C_2H_2 l / h	HCN l / h	HAK	HCN	Bx	BA	AA	Xp			
one	2	3	4	5	6	7	eight	9	10	eleven	12	thirteen	14	15
one	SiS1-40 NMP-50 DMF-10	eleven	130	38.0	4.8	10.59	0.04	2.50	3.84	0.06	0.20	17.54	61.60	107.0
		15	130	34.0	5.3	11.06	0.10	2.78	2.88	0.13	0.15	15,70	65.06	98.2
		eighteen	130	51.0	5.3	12.00	0.24	0.83	1.32	0.13	0.05	31.94	83.74	140.7
		twenty	130	40.0	5.3	11.16	track.	1.17	4.70	0.09	0.16	19.80	64.58	113.2
		22	130	34.0	5.3	11.10	track.	2.16	3.05	0.11	0.13	15.75	67.07	98.2
2	CuC1-40 NMP-50 DMF-9.9 AgCl-0.1	9	132	57.0	4.9	7.32	0.44	1.14	2.38	Sl.	off.	17.13	67.53	136.0
		thirteen	132	57.0	4.9	8.92	0.35	1.05	2.42	Sl.	off.	20.87	71.99	136.0
		21	130	57.0	5.0	9.66	0.27	0.76	2.06	0.05	off.	22,60	77.09	136.3
		37	129	53.5	3.8	9.49	0.21	0.85	1.56	0.06	off.	21.96	79.34	125.9
3	CuC1-40 NMP-50 AgCl-0.1 H_3PO_4-0.1 DMF-9.8	5	128	56.7	3.6	9.15	0.12	1.69	3.34	0.13	0.25	23.19	62.84	150.7
		eleven	129	57.5	4.6	10.11	sl.	0.66	2.87	0.13	0.07	23.91	73.05	155.2
		14	129	60.4	4.3	8.96	sl.	1.06	1.88	0.18	0.06	22.71	73.81	161.2
		27	121	50.0	2.4	9.42	3.61	1.42	0.02	sl.	off.	26.53	86.74	131.0
		29	122	48.3	2.0	8.45	0.74	1.62	0.10	sl.	sl.	21.42	83.08	125,7
4	CuC1-40 NMP-50 DMF-10 HCl-4	5	119	44.4	2.5	7.23	0.38	0.81	0.30	1.92	off.	17.96	70.46	117.2
		eight	118	50.5	2.5	6.74	0.52	0.65	0.30	1.75	off.	17.94	71.40	132.5

The catalyst base in non-aqueous media is a mixture of honey chloride (I) and N-methyl pyrrolidone (NMP) and dimethylformamide (DMF).

The catalyst was prepared as follows: the required amounts of NMPa and DMF were mixed, the necessary additives were added, and then CuCl was added. Catalyst composition CuCl-NMP-DMF, as well as with such additives as conc. hydrochloric acid, silver chloride, and silver chloride together with phosphoric acid are not a homogeneous solution, but a suspension of dirty green color. When standing, green copper chloride settles down, and a layer of dirty green solution remains at the top. Before pouring the heated catalyst, it was well stirred and poured. In this case, what was in the flask got into the reactor. And only the catalyst, in which trichloroacetic acid (CCI_3COOH) was added as an additive, is a homogeneous solution. The reaction mixture was monitored by chromatographic methods. The reactions were carried out at a temperature of 120-130 ^{0}C. CuCl-NMP-DMFA.

In the catalyst [CuCl-NMP-DMFA-CCl_3COOH] of this composition, copper chloride is in a dissolved state. Two syntheses were carried out : a) the first within 54 hours; b) the second within 40 hours. It was impossible to conduct the process stably at a given HCN breakthrough (0.2-0.5). At first, at a high consumption of acetylene for the evaporation of hydrocyanic acid (up to 27 l / h), there was no HCN in the reaction gas for 13 hours, and at 27 hours of catalyst operation with a minimum consumption of acetylene (1 liter or less), the breakthrough of HCN reached 7.4% ... During the work, many polymers were formed. The boiling of the synthesis products in the refrigerator was observed, therefore it was necessary to reduce the temperature or the consumption of acetylene. The table shows that, as in the above described batch of catalyst, the higher the consumption of acetylene, the higher the activity and selectivity of the catalyst. Thus, at a flow rate of 52.5 l / h, the activity of the catalyst is 13.99 hl / h, the selectivity is 46.45% at a flow rate of 45-47 l / h. activity 21.29-21.81 g / L hour, selectivity up to 92%.

As can be seen from the data in Table 2, the activity of the catalytic system CuCl - NMP - DMF is twice as high as that of aqueous solutions of CuCl. At a acetylene consumption of 34-40 l / h, the content of NAC in the reaction gas is 10.59-11.16%, the activity of the catalyst is from 15.7 to 19.8 g / l / h, the selectivity is 61.6-67.07 %. At a flow rate of 50-51 l / h, the content of NAC is 12.0-12.66%, the activity is 30.00-31.94 g / l / h, the selectivity is 83.74-83.90%. Apparently, at a high consumption of acetylene, good mass transfer is ensured and the rate of formation of NAC increases.

CONCLUSIONS

1. The introduction of $ZnSO_4$ and ZnO additives into the shop catalyst, under these conditions, did not give a positive effect
2. Research of catalysts in non-aqueous media leads to an increase in their activity and selectivity in comparison with aqueous media. It was shown for the first time that the composition of the CuCl - NMP - DMF catalyst is characterized by high activity (up to 32 g / l. H.) And selectivity (83-90%), i.e. the activity of this composition is twice as high as compared to the water-shop ones (12-18 g l.h.).

REFERENCFES

I. Fayzullaev NI, OmanovB.Sh., Musulmonov N.KhBifunctional catalyst lard acetylenning catalyst Yzgarishlari. Monograph. Samarkand 2019
II. Fayzullayev NI, Omanov B.SH. Physiochemical characteristics of the catalysts Monografiapokonferencyjna " Science, research, development # 26/8 ". Berlin. 03/15/2020. PP. 172-177
III. Markova N.N., Afanasyeva E.A. Acrylonitrile production. M. 1965.
IV. American Pat. 3.340207 (1981)
V. Temkin S.N., Shestakov T.K., Treger Yu.A. Acetylene: Chemistry; Reaction mechanisms; Technology M. 1991