water distillation. It is showin that the nature of amidating agent determines the composition of reaction products: at amination of DA **I** with unsubstituted carbamide the main product is imide **IVa**, and at amination with substituted carbamides and amines the main products are corresponding monamides **IIIb-f**. On the basis of experimental data the mechanism of reaction is suggested.

The analysis of experimental data allows us to state that the reaction of amination occurs through the connection of isocyante molecule, being a product of carbamide dissociation, to diphenic acid. Then a molecule of CO_2 is ejected from the intermediate acylurethane and the corresponding monamide is formed, which is cyclized into imide, when losing a molecule of H_2O.

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PROCESS OF CATALYTIC SYNTHESIS OF ACETONITRILE FROM ACETIC ACID AND AMMONIA AT γ–Al$_2$O$_3$

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In the reaction of catalytic synthesis of acetonitrile from acetic acid and ammonia the influence of ratio of reagents, reactor temperature, addition of acetic acid, acetic anhydrite and acetamide into the reaction mixture of ethyl ether as well as catalyst promotion (γ-Al$_2$O$_3$) by phosphoric acid on the parameters of the process. Optimal conditions of the reaction are determined and the scheme of commercial prototype process is suggested.

Acetonitrile is widely used in organic synthesis as an intermediate reagent, solvent, azeotrope — forming at substances separation [1, 2], as well as at synthesis of CN_x nanotubes [3]. In industry acetonitrile is produced as a by-product of acrylonitrile synthesis. Processes directed at target synthesis of acetonitrile become perspective because of increasing requirement of acetonitrile in petrochemical syntheses. Methods of acetonitrile obtaining from ammonia and acetic acid, alcohols, paraffins and olefines [4] are developed. Syntheses from alcohols, paraffins and olefines are characterized by insufficient selectivity and low process productivity. Until recently none of methods of purposeful acetonitrile synthesis is realized in industry.

Synthesis of acetonitrile from acetic acid is perspective for realization owing to little consumptions for separation and purification of a target product. Well-known syntheses of acetonitrile from acetic acid and ammonia [4–6] were carried out in tubular reactors with volume velocity of acid supplying 0,3 h^{-1} or 0,008...0,060 mole/sec·l acetonitrile yield higher than 80 % was observed at temperatures 440...480 °C. But carrying out the reactions at above mentioned temperatures results in thermal pyrolysis of an acid and products of synthesis with catalyst carbonizing and desired product — acetonitrile- contamination, besides high expenditure of energy for reactor heating. At high temperatures formation of hydrocyanic acid is possible when using steel reactor.

Synthesis process temperature decreasing to 350...380 °C is perspective due to the fact that water vapor may be used instead of furnace gases for reactor heating.
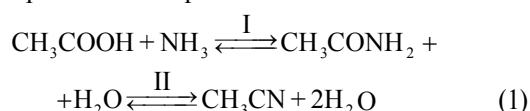
Thus, the aim of the given paper is to examine the influence of the following factors: variation of reagents ratio; reactor temperature; reaction mixture dilution; catalyst promotion on the catalytic synthesis reaction of acetonitrile from acetic acid. According to obtained regularities to suggest optimal conditions for carrying out the reaction of acetonitrile with high productivity obtaining.

Experiments

The investigations were carried out in a flow steel (12X18H10T) reactor with reagents incoming flow at prior heating of reaction mixture to reaction temperature. Ratio NH_3:CH_3COOH varied in the range 1,5...5,0, reaction temperature − 350...450 °C, load for acetic acid and acetamide 0,49...1,02 g/sm³·h. The presented contact time was calculated as ratio of catalyst volume to volume velocity of steam-and-gas mixture at reaction temperature. Ethyl ether of acetic acid and acetic anhydride of «ch.p.» qualification were added into reaction mixture at 5 wt. %. The analysis of synthesis products (H_2O, NH_3, CH_3COONH_4, CH_3CN, CH_3CONH_2, CH_3COCH_3, CH_2O and HCN) was carried out chromatographically (chromatograph LChM-80) using sorbent Separon SDA, detector-katharometer, carrier gas-helium. The percent of compaction products (% CP) was determined as a ratio of generating sealing products to catalyst mass on 1 sm³ of transmitted acid. γ-Al_2O_3 (A-64, S_{sp}=205 m²/g, total volume of pores is 0,68 sm³/g) and γ-Al_2O_3 promoted with phosphoric acid of «ch.p.» qualification at the rate of 2...6 wt. % were used as catalysts.

Results and their discussion

Acetonitrile formation from acetic acid and ammonia is equilibrium two-phase reaction:

$$CH_3COOH + NH_3 \underset{}{\overset{I}{\rightleftharpoons}} CH_3CONH_2 +$$

$$+H_2O \underset{}{\overset{II}{\rightleftharpoons}} CH_3CN + 2H_2O \qquad (1)$$

The calculation of thermodynamic functions and equilibrium constant for phases I and II (scheme 1) given in the paper [7] showed that the reaction of acetamide formation from acetic acid and ammonia in the range of temperatures 250...450 °C is weak-exothermic (ΔH_{av}=−2,18 kJ/mole), Gibbs's energy (Δ=−(3,56...4,22) kJ/mole) and equilibrium constant (C_{eq}=2,76...2,26) change insignificantly in comparison with reactions temperature. Phase II of acetamide dehydration is endothermic ΔH_{av}=84,37 kJ/mole, according to the given calculations, equilibrium constant becomes more than 1 at temperature higher than 320 °C. Thus, the completeness of reaction of acetic acid ammonolysis may be reached by: a) rise of reactor temperature (restriction − thermal decomposition of acetic acid and reaction products); b) rates variation of ammonia and acetic acid supply (acetic acid load). The improvements of catalytic characteristics of the process by means of side reactions decrease may be also reached by catalyst promoting with admixtures of different nature.

a) Influence of reaction temperature and reaction mixture composition

Reactor temperature increase higher than 400 °C allows obtaining acetonitrile high yield at large loads for acetic acid, but at the same time a part of non-target reactions increases − decarboxylation of acetic acid to acetone and CO_2, and also sealing products formation on catalyst surface with its activity decreasing. After 5 hours of work at temperature 440 °C acetonitrile yield decreases from 98,5 to 91,5 %. Reaction temperature decrease to 350...380 °C allows to reduce significantly the amount of formed of compaction products (CP) (from 0,19 at 400...450 °C to 0,04 at 350...380 °C) (table) and to prolong the catalyst period of work.

In the given process catalyst carbonization starts from the initial part of catalyst layer in the coarse of reaction mixture, tail end of the layer is less and last carbonized. Probably, it is connected with storage of water, generating during the reaction, in reaction gases and decrease of acetic acid concentration-the main source of CP. One of the methods of catalyst carbonization decrease may be water vapors introduction into reaction mixture, but as it was mentioned in [6] use of diluted acetic acid results in decrease of acetonitrile yield and catalyst productivity. Therefore it is justified to add into reaction mixture substances which would decrease rate of CP formation and at the same time participate in reaction with target product formation, for example: acetamide, ethyl acetate or acetic anhydride.
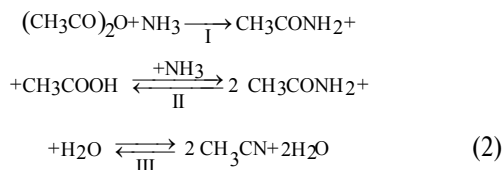
Table. *Influence of temperature and reaction mixture composition on CP formation and productivity (P) of sample*

T, °C	Reaction mixture composition	% CP	Acetonitrile yield, %	P
400...460	CH_3COOH	0,19	75,2	0,425
350...400	CH_3COOH	0,04	68,7	0,535
	CH_3CONH_2	0,03	80,7	0,489
	CH_3CONH_2+NH_3	0,03	97,8	0,643
	95 % CH_3COOH+ 5 % $(CH_3CO)_2O$	0,02	83,1	0,546
	95 % CH_3COOH+ 5 % $CH_3COOC_2H_5$	0,73	67,5	0,215

% CP is the percent of compaction products from catalyst weight per 1 sm³ of feeding acid; P is the acetonitrile productivity of catalyst, kg/dm³·h

Addition of ethyl acetate to acetic acid promotes higher coal deposit, in comparison with pure acetic acid (table). Use of mixture of acetic acid and 5 wt. % of acetic anhydride at equal values of yield of acetonitrile decreases catalyst carbonization. Using the mixture of acid with anhydride in the reaction insignificant rise of conversion is observed, in this case yield of acetonitrile increases due to selectivity increase of desired product − acetonitrile.

Probably, it is connected with the fact that when introducing acetic anhydride into reaction mixture besides the reactions (scheme 1) the interaction reaction of acetic anhydride and ammonia occurs (scheme 2):

$$(CH_3CO)_2O + NH_3 \xrightarrow{I} CH_3CONH_2 +$$

$$+CH_3COOH \underset{II}{\overset{+NH_3}{\rightleftarrows}} 2\ CH_3CONH_2 +$$

$$+H_2O \underset{III}{\rightleftarrows} 2\ CH_3CN + 2H_2O \qquad (2)$$

Catalyst carbonization decrease at 5 wt. % of acetic anhydride addition may be explained by high acetatical capacity of the latter: acetic anhydride when interacting with sealing products converts them into volatile compounds removed from catalyst surface.

Synthesis of acetonitrile from acetamide (intermediate product) by γ-Al$_2$O$_3$ is accompanied by the processes of hydration and acetamide decomposition with ammonium acetate and methylamine generatiom (table). Introduction of ammonia into reaction mixture fully suppresses side reactions and increases acetonitrile yield. In this case, the degree of catalyst surface carbonization is lower in comparison with acetic acid. It confirms the assumption that the main source of CP is acetic acid.

b) Influence of feed rate of acetic acid and ammonia

In the range of temperatures 350...400 °C the formation of sealing products is lower, but it is necessary to decrease the load for acetic acid (to increase contact time) for increasing of reagents conversion degree, that may results in rise of a part of side reactions: so, at load for acid 0,58 g/sm^3·h selectivity of acetone formation is 0,6 %, but at 1,02 g/sm^3·h and temperatures 350...380 °C acetone is not found out in the reaction products. Thus when using the catalyst γ-Al$_2$O$_3$ optimal load for acetic acid (0,8...1,02 g/sm^3·h) and temperature (350...380 °C), at which a part of side reactions at high putout of acetonitrile is minimal are determined.

One more parameter influencing the process of acetic acid ammonolysis may be a variation of reagents partial pressures.

Stoichiometrically reaction of acetonitrile formation from acetic acid and ammonia occurs at mole ratio ammonia/acid − 1:1, but in the range of temperatures 350...380 °C it is shown that increase of ammonia content in mixture results in rise of acetic acid conversion and selectivity of acetonitrile and as a result increase of acetonitrile output in spite of a given contact time decrease is observed (fig. 1).

It is, probably, connected with increase in ammonia partial pressure shifting the equilibrium in the direction of acetamide formation (reaction I, scheme 1) with subsequent formation of acetonitrile (reaction II). Increase of ammonia partial pressure at reactor temperature higher than 400 °C does not influence much values of selectivity and acetonitrile yield.

Thus, it may be noticed that at optimal load for acetic acid (0,8...1,02 g/sm^3·h) and temperatures (350...380 °C) ammonia partial pressure increase (or ammonia feed rate) promotes rise of acetic acid conversion and yield acetonitrile, in spite of contact time decrease from 1,75 s at ratio ammonia/acid − 1,5:1 to 0,89 s at ratio ammonia/acid − 4:1.
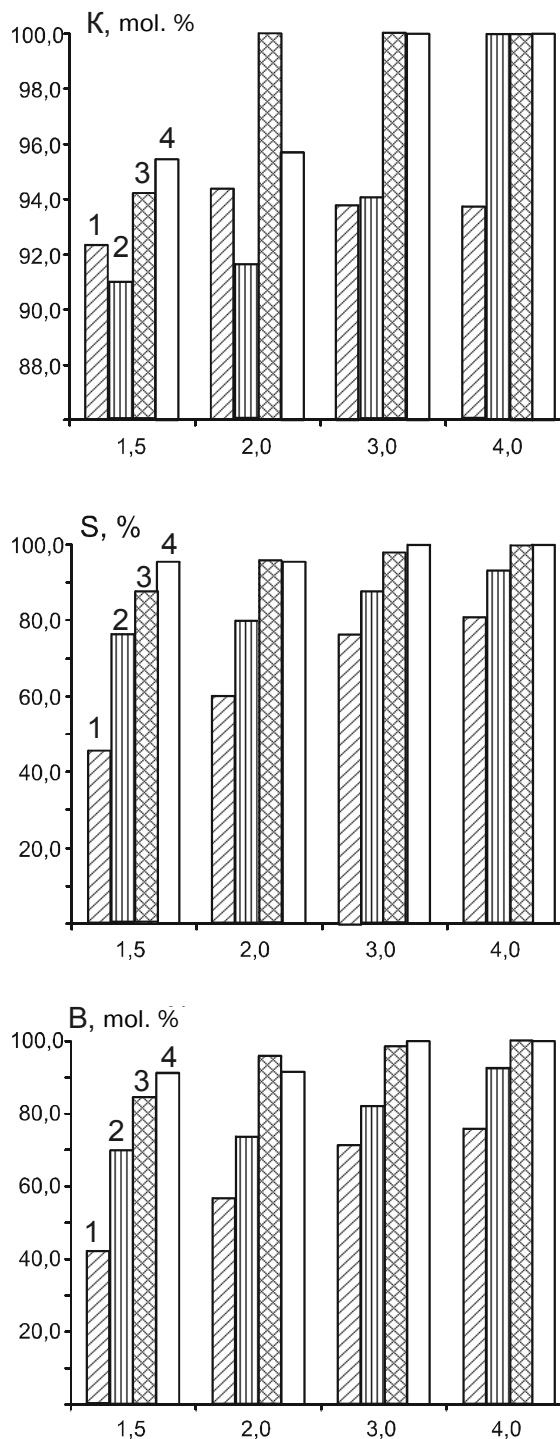

Fig. 1. Acetic acid conversion (C, mole %), selectivity of acetonitrile (S, %) and its yield (Y, mole %) depending on ammonia/acetic acid ratio and temperature: 1) 350; 2) 360; 3) 370; 4) 380 °C

c) Influence of catalyst promoting

Another method of compaction products formation decrease and process intensification may be aluminium oxide promoting. Promoting of γ-Al$_2$O$_3$ with 2 wt. % of phosphoric acid increases selectivity and acetonitrile output, without practically changing acetic acid conver-

sion. Further increase of amount of promoting admix-
ture- phosphoric acid (to 6 wt.%) allows rising selectivi-
ty and acetonitrile yield by means of increase of acetic
acid transformation degree. It is seen from fig. 2 that on
the γ-Al$_2$O$_3$ sample at 380 °C selectivity of acetonitrile
~90 % (yield=87,3 %) is observed and for γ-Al$_2$O$_3$ pro-
moted one with 6 wt% phosphoric acid already at
350 °C selectivity is 93 % (yield =90,8 %).

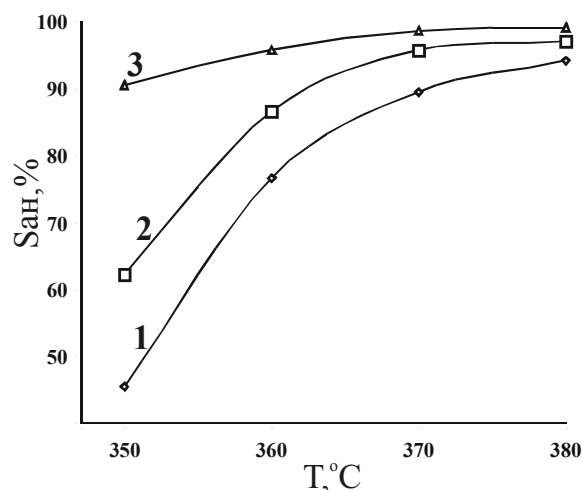**Fig. 2.** *Dependence of selectivity of acetonitrile on reactor tem-*
perature at catalysts: 1) γ-Al$_2$O$_3$, 2) 2 wt. % H$_3$PO$_4$/γ-Al$_2$O$_3$,
3) 6 wt. % H$_3$PO$_4$/γ-Al$_2$O$_3$

Thus, using of catalysts promoted with phosphoric
acid allows decreasing temperature of process carrying
out that in its turn results in decrease of carbonization
degree of catalyst surface and thereby promotes increase
of inter-regeneration time of catalyst operating: so, for
H$_3$PO$_4$/γ-Al$_2$O$_3$ catalysts at service temperature
350...380 °C % CP amounts to 0,020...0,019 and for
non-promoted γ-Al$_2$O$_3$ % SP=0,040. It is connected
with the fact that γ-Al$_2$O$_3$ promoting with phosphoric

acid increases contacts total acidity and in this case re-
distribution of acid sites by force occurs: concentration
rise of sites with the force $3,3 \geq H_o > 2,0$ (the Bronsted's
acid centers) and decrease of sites with the force $2,0 \geq H_o$
(probably, the Lewis's acid centers) where compaction
products formation observed [8]. γ-Al$_2$O$_3$ phosphoric
acid treatment promotes a number of active centers of
acetamide dehydration increasing and, as a result, acce-
leration of reaction equilibrium achievement that res-
ults in increase of acetonitrile selectivity and producti-
vity of desired product – acetonitrile to 0,71 kg/dm^3·h
at 370 °C.

Conclusions

When using catalysts A-64 promoted with phospho-
ric acid and ratios NH$_3$:CH$_3$COOH=(3...4):1 in the
process of acid ammonolysis it is possible to achieve the
productivity of acetonitrile 0,7...0,8 kg/dm^3·h, minimi-
zing formation of by-products to 0,1 % per reacted acid.
Optimal temperature interval of reaction is 350...400 °C
(at temperatures higher than 400 °C contribution of py-
rolysis and acetic acid decarboxylation reactions incre-
ase). In connection with high reaction endothermic it
was proposed before to use tubular reactors of complex
construction. Using of single-layer adiabatic reactor is
not possible because of restrictions at reaction mixture
heating higher than 400 °C as side reactions may occur
homogeneously on heat exchangers walls forming resins
and carbon. Application of multilayer reactor with layer
feeding of ammonia heated to 400...410 °C allows avoi-
ding this restriction. In the case of three-layer device the
scheme may be like this: 1:1,5 acid ammonia ratio is fed
to the first layer of catalyst, to the following layer heated
ammonia is fed in 1,0...1,5 ratio to acetic acid initially
supplying to the reactor, and so on, while total sum ra-
tio NH$_3$:CH$_3$COOH (4,0...4,5):1 being achieved that
conforms to the determined optimum.

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