



XV International Scientific Conference “Chemistry and Chemical Engineering in XXI century”  
dedicated to Professor L.P. Kulyov

## The Process of Acetonitrile Synthesis over $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Promoted by Phosphoric Acid Catalysts

Sergey I. Galanov<sup>a\*</sup>, Olga I. Sidorova<sup>a</sup>, Mikhail A. Gavrilenko<sup>b</sup>

<sup>a</sup>Tomsk State University, 36, Lenin Ave., 634050, Tomsk, Russia

<sup>b</sup>Tomsk Polytechnic University, 30, Lenin Ave., 634050, Tomsk, Russia

### Abstract

The influence of principal parameters (reaction temperature, ratio of acetic acid and ammonia, composition of reactionary mixture and promotion of catalysts) on the selectivity and yield of the desired product was studied in the reaction of catalytic acetonitrile synthesis by ammonolysis of acetic acid. The processing of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by phosphoric acid increases amount of the centers, on which carries out reaction of acetamide dehydration. The kinetic model of a limiting stage of reaction – the acetamide dehydration to acetonitrile was suggested. In the process of ammonolysis of acetic acid it was demonstrated that the use of catalysts promoted by phosphoric acid and ratio NH<sub>3</sub>:CH<sub>3</sub>COOH=(3-4):1 at temperatures of a reactor 360-390 °C leads to the increase of acetonitrile productivity to 0.7-0.8 g/cm<sup>3</sup>·h and allows to minimize formation of by-products.

© 2014 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of Tomsk Polytechnic University

**Keywords:** Catalyst, synthesis of acetonitrile, alumina, acetic acid, acetamide

### 1. Introduction

Acetonitrile is widely used in organic synthesis as an intermediate reagent, solvent, azeotropizer and in highly effective liquid chromatography a mobile phase<sup>1-3</sup>. Acetonitrile is commercially produced as a by-product of acrylonitrile synthesis<sup>4</sup>. Therefore the investigation and development of inexpensive and commercially convenient methods for acetonitrile production represent an urgent problem. Acetonitrile synthesis from acetic acid is more promising due to less expense for isolation and purification of the desired product. In the past acetonitrile synthesis from acetic acid and ammonia was carried out in the tubular reactors<sup>5,6</sup> or from alcohols<sup>7,8</sup>, acetonitrile yield above 80 % was observed at the temperatures of 440-480°C. But the reaction carried out at these temperatures, along with

\* Corresponding author: Sergey I. Galanov. Tel.: +7-3822-420-386

E-mail address: [galanov@xf.tsu.ru](mailto:galanov@xf.tsu.ru)

high energy expenses for reactor heating, leads to thermal pyrolysis of acid (or products of synthesis) followed by catalyst carbonization and contamination of the desired product. At the increased temperatures with use of steel reactors formation of a hydrocyanic acid is observed.

The reaction of acetic acid ammonolysis is very interesting because of its being one of brightest representatives of reactions in the acid-basic catalysis. In an interval of reaction temperatures the side reactions of decarboxylation acetic acid up to acetone, the decomposition of acetic acid up to pitches and carbon, the formations of amines and a hydrocyanic acid are thermodynamically possible at interaction with ammonia. Therefore the selection of optimum conditions of synthesis at the maximal acetonitrile yield with the minimal maintenance of by-products is an actual problem.

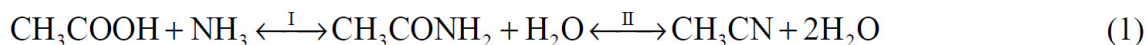
## 2. Experimental

The catalysts used were  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $S_{\text{spec}}=149$  m<sup>2</sup>/g, total pore volume is 0.68 cm<sup>3</sup>/g) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> promoted by phosphoric acid (2-6 % mass) and 2 mass% Ca(OH)<sub>2</sub>.

The study was made in a flow steel reactor<sup>9</sup> with an upward reagent flow at a preheating of the reaction mixture up to the reaction temperature at maximal volume of the catalyst equal to 45 cm<sup>3</sup>. The ratio NH<sub>3</sub>:CH<sub>3</sub>COOH at catalytic experiments varied in interval from 1.5 to 6.0, the temperature of reaction - 320-450°C, the loading on acetic acid and acetamide is 0.49-1.5 g/cm<sup>3</sup>·h. The reduced contact time (s) was calculated as the relationship between the catalyst volume and the space velocity of the gas-vapour mixture at the reaction temperature. The acid properties of a surface of catalytic samples determined by a technique of indicator no aqueous titration<sup>10</sup>. The quantity of the acid centers found a way of titration by solution benzyl amine (C=0.01M) of suspension of powder of the catalyst with previously adsorbed indicator in drained n,n-dimethylformamide. The quantity of benzyl amine, gone to titration, defines quantity of the acid centers (μmol/g) which have acid force, big or equal a pKa of the used indicator. % CP is the percentage of the compaction products formed per catalyst weight per 1 cm<sup>3</sup> of the acid input.

## 3. Results and discussion

The process of acetonitrile formation from acetic acid and ammonia is equilibrium two-stages reaction<sup>11</sup>:



The calculation of thermodynamic functions<sup>12</sup> showed that the reaction of acetonitrile formation by ammonolysis of an acetic acid is endothermic:  $\Delta H_{\text{av}}=82.06$  kJ/mol at temperatures 200-450 °C, with lg of equilibrium constant > 0 at temperature above 300 °C (figure 1, №1). The calculation of thermodynamic functions and constant of equilibrium for stages I and II (scheme 1) showed that the reaction of acetamide formation from an acetic acid and ammonia (at temperatures 250–450 °C) is weakly exothermal:  $\Delta H_{\text{av}} = -2.18$  kJ/mol,  $\Delta G$  and  $K_p$  is not changed in the considered interval of temperatures 250-450°C. The stage II – dehydration of acetamide is endothermic:  $\Delta H_{\text{av}}=84.37$  kJ/mol,  $\Delta G<0$  at temperature above 320°C. (figure 1, № 2). In literature the question on a limiting stage of process is not considered, but the identical change of the designed constants of equilibrium for total reaction (figure 1, №1) and stage II (figure 1, №2) can show that at temperatures 330-400 °C the dehydration of acetamide is a limiting stage.

In case of a flowing reactor with a stationary mode of submission of reagents the increase in temperature of a reactor higher than 400 °C results in a high yield of acetonitrile at the big loading on acetic acid, the productivity on acetonitrile is equal to 0.89 g/cm<sup>3</sup>·h. But in this case: the decarboxylation of acetic acid to acetone and CO<sub>2</sub> and formation of pitches and of compaction products (CP) on the surface of the catalyst were observed, its activity decreasing. Thus, due to catalyst carbidization, at temperature 440°C acetonitrile yield changed from 98.5 to 91.5 % within 5 hours of operation. The reduction in reaction temperature allows one to significantly decrease the amount of the compaction products (CP) formed (from 0.19 at 400-450°C to 0.04 at 350-380°C) and to extend the catalyst life between regenerations.

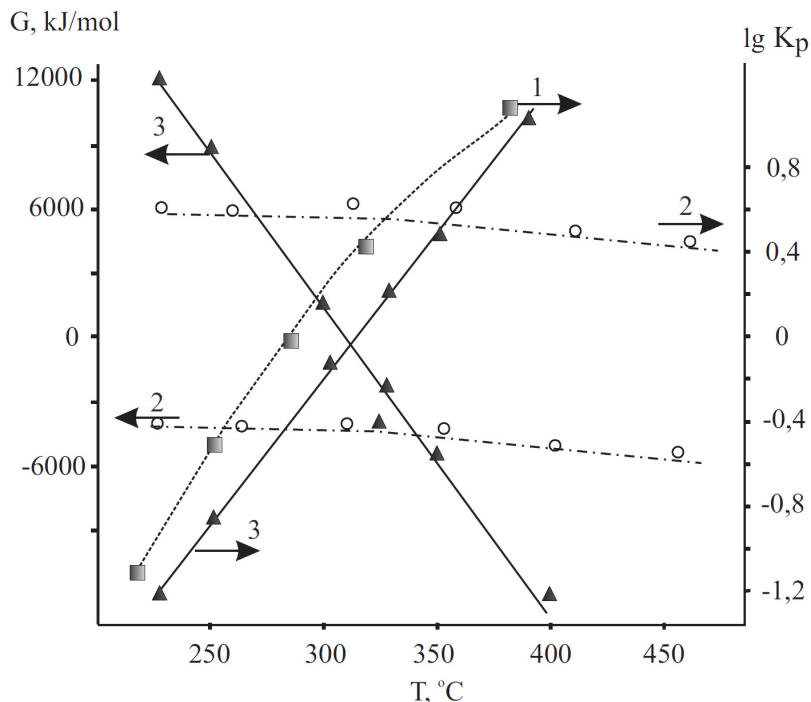


Fig.1 Temperature dependence of free energy of reaction ( $\Delta G$ ) and constants of equilibrium (1 – total reaction; 2 – reaction of acetamide formation from acetic acid and ammonia; 3 – acetonitrile formation from acetamide)

At temperatures 350-400 °C formation of products of condensation is less, but for increase in a degree of transformation of reagents it is necessary to reduce loading on acetic acid (to increase time of contact); it can result in increasing a share of side reactions: thus, at loading on acetic acid 0.58 g/cm<sup>3</sup>·h, selectivity of acetone formation is equal to 0.6 %, but at 1.02 g/cm<sup>3</sup>·h and at temperatures 350-380 °C acetone in products of reaction is not found. Optimum loading on acetic acid (0.8-1.02 g/cm<sup>3</sup>·h) and temperatures (350-380°C) at which the share of side reactions is minimal at a high acetonitrile yield (table 1) are determining for the catalyst  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

The reaction of acetonitrile formation from acetic acid and ammonia proceeds at molar ratio ammonia:acid = 1:1. But at temperatures 350-380°C it was shown that the increase in the contents of ammonia in a mix results in increasing growth of acetonitrile yield despite of reduction of contact time (table 1). The increase in the partial pressure of ammonia shifts the equilibrium towards acetamide formation (reaction I, scheme 1) followed by acetonitrile formation (reaction II). At temperature of a reactor higher than 400 °C the increase partial pressure of ammonia practically does not influence selectivity and acetonitrile yield.

The study of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> promoted by base - Ca(OH)<sub>2</sub> and acid - H<sub>3</sub>PO<sub>4</sub> shows that the increase in basicity of catalysts surface leads to the inhibition of stage II (scheme 1) in reaction of acetic acid ammonolysis<sup>5</sup>. In this case the basic product of reaction is acetamide. The promotion of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by 2 mass % of phosphoric acid does not change conversion of acetic acid, but increases selectivity and acetonitrile yield. The increase in amount of phosphoric acid to 6 mass % results in increasing selectivity and acetonitrile yield due to increase in a degree of transformation of acetic acid (table 1). Thus, the use of catalysts promoted by phosphoric acid allows to lower temperature of carrying out the process that results in decreasing a degree of the compaction products formation on surfaces of the catalyst and promotes to increase in time of operation catalyst: for example, for H<sub>3</sub>PO<sub>4</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts at temperatures of operation 350-380°C %CP is equal to 0.020-0.019, and for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> %CP=0.040.

Table 1. The influence of reactor temperature and a ratio of reagents on catalytic parameters of reaction

$T_{in}, ^\circ C$	$Q, g/cm^3 \cdot h$	Ration $NH_3:CH_3COOH$	$\tau_{red}, c$	K, %	$S_{CH_3CONH_2}, \%$	$S_{CH_3CN}, \%$	$B_{CH_3CN}, \%$
$\gamma-Al_2O_3$							
350	1.02	1.5	1.75	88.5	37.8	62.2	55.1
350	1.02	2.0	1.50	92.1	25.4	74.6	68.7
350	1.02	3.0	1.10	92.0	13.9	86.1	79.2
350	1.02	4.0	0.89	92.2	10.8	89.2	82.2
360	1.02	1.5	1.75	88.6	23.4	86.6	76.7
360	1.02	2.0	1.50	89.6	20.0	88.8	79.5
360	1.02	3.0	1.10	92.9	12.2	93.4	86.8
360	1.02	4.0	0.89	99.9	7.4	96.1	96.1
360	0.49	2.0	3.13	100	-	99.3	99.4
360	0.58	2.0	2.68	99.2	-	99.4	98.7
360	0.67	2.0	2.30	99.2	-	99.5	98.5
380	1.02	1.5	1.75	99.5	4.5	95.5	95.0
380	1.02	2.0	1.50	99.5	3.0	97.0	97.0
2 mass % $H_3PO_4/\gamma-Al_2O_3$							
360	1.02	2.0	1.50	92.9	11.2	74.6	66.7
360	1.02	3.0	1.10	93.1	6.6	86.1	79.2
360	1.02	4.0	0.89	93.8	3.9	89.2	82.2
6 mass % $H_3PO_4/\gamma-Al_2O_3$							
360	1.02	2.0	1.50	95.9	2.9	93.2	89.4
360	1.02	3.0	1.10	98.1	2.5	95.7	93.9
360	1.02	4.0	0.89	98.6	1.1	96.3	95.0
2 mass % $Ca(OH)_2/\gamma-Al_2O_3$							
360	1.02	2.0	1.50	94.6	72.3	26.2	24.7

$\tau_{red}$  is the reduced contact time at the reaction temperature, s

$Q$  is the acetic acid load,  $g/cm^3 \cdot h$

K - acetic acid conversion, (mol %)

$S_{CH_3CONH_2}$ ,  $S_{CH_3CN}$  is respectively acetamide and acetonitrile selectivities (%)

$B_{CH_3CN}$  is acetonitrile yield (mol %)

In other words the promotion of  $\gamma-Al_2O_3$  by phosphoric acid increases the total acidity of contacts, thus there is a redistribution of the acid centers on force: the increase of concentration of the centers with force  $3.3 \geq H_0 > 2.0$  (Brönsted's acid centers) and the decrease in amount of the centers with force  $2.0 \geq H_0$  (probably Lewis's acid centers) on which there is a formation of condensation products (table 2) is observed. Processing of  $\gamma-Al_2O_3$  by phosphoric acid promotes to the increase in quantity of the active centers on which the dehydration of acetamide that results in increasing selectivity and productivity of acetonitrile to  $0.710 g/cm^3 \cdot h$  ( $T=370^\circ C$ ), in so doing the promotion by phosphoric acid leads to the block of centers of the compaction products formation.

Table 2. The acid property of catalyst

Catalyst	The concentration of acid center, micro mol of benzylamine/g of catalyst					
	$4.8 \geq H_0 > 3.3$	$3.3 \geq H_0 > 2.0$	$2.0 \geq H_0 > 1.3$	$1.3 \geq H_0 > 0.8$	$0.8 \geq H_0$	$\Sigma$
$\gamma-Al_2O_3$	81.0	12.7	57.2	0.7	4.2	155.8
2 mass % $H_3PO_4/\gamma-Al_2O_3$	88.5	52.0	22.0	0.5	4.5	167.5
6 mass % $H_3PO_4/\gamma-Al_2O_3$	58.0	99.0	16.0	-	3.0	176.0
* $\gamma-Al_2O_3$	14.0	5.0	12.0	-	-	31.0
*2 mass % $H_3PO_4/\gamma-Al_2O_3$	34.0	13.0	14.0	-	-	61.0
*6 mass % $H_3PO_4/\gamma-Al_2O_3$	51.0	16.5	17.5	-	-	85.0

\*Catalysts after reaction. Amount of products of condensation from weight of a sample is 6.4–6.8 %

The study of dehydration reaction of an intermediate product – the acetamide has shown that synthesis of acetonitrile from acetamide on  $\gamma-Al_2O_3$  is accompanied by reverse reaction of hydrolysis to ammonium acetate (table 3).

Table 3. The influence of reactor temperature and composition of reactionary mixture on catalytic parameters of acetamide dehydration reaction over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> promoted by phosphoric acid

The catalyst	Initial reagents	T, °C	K, %	S <sub>CH<sub>3</sub>CN</sub> , %	B <sub>CH<sub>3</sub>CN</sub> , %	S <sub>CH<sub>3</sub>COONH<sub>3</sub></sub> , %
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	acetamide	360	79.7	85.5	68.1	12.0
		380	93.1	80.2	74.7	16.4
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	acetamide/ammonia =1:1.5	360	92.0	97.4	89.6	2.5
		380	98.3	99.5	97.7	0.5
6 mass % H <sub>3</sub> PO <sub>4</sub> / $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	acetamide/ammonia =1:1.5	360	99.5	100	99.5	-
		380	100	100	100	-

The introduction of ammonia in a reaction mix reduces speed of reverse reaction of hydrolysis due to: shift of the equilibrium towards acetamide formation (reaction I, schema 1) followed by acetonitrile formation (reaction II); and competitive adsorption of ammonia and products of reaction (water and acetonitrile). The promotion of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by phosphoric acid promotes to the increase in conversion of acetamide acetonitrile yield to 100 %. The kinetic model, which takes into account competitive adsorption of ammonia and reaction of acetamide hydrolysis was suggested for the reaction of the acetamide dehydration.

$$w = k \cdot K_A \cdot p_A \left( \frac{1 + K_{NH_3} p_{NH_3} - K_{H_2O} \cdot (p_{H_2O})^{1/2}}{K_A \cdot p_A + K_{H_2O} \cdot p_{H_2O} + K_{NH_3} \cdot p_{NH_3}} \right) \quad (2)$$

The energy of desorption activation for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 6 % H<sub>3</sub>PO<sub>4</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is equal to 63.2 and 58.3 kJ/mol, accordingly.

#### 4. Conclusion

The processing of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> by phosphoric acid increases the amount of the centers of acetamide dehydration that allows speeding up achievement of equilibrium in limiting stage of process – the acetamide dehydration and blocks the centers of the compaction products formation.

The use of catalyst promoted by phosphoric acid and ratios NH<sub>3</sub>:CH<sub>3</sub>COOH = (3-4):1 in the process of acetic acid ammonolysis allows to achieve acetonitrile productivity 0.7-0.8 g/cm<sup>3</sup>·h, to minimize by-products formation up to 0.1 % on the reacted acid at temperatures 360-390 °C. But the big amount of water formed per unit of a target product can complicate the process of release and rectification of acetonitrile. Therefore for synthesis of acetonitrile from acetic acid and ammonia the use of two-reactor circuit with intermediate extraction of acetamide can be perspective. In the first reactor the use of the catalyst -  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> promoted by the base at temperatures 290-340 °C makes possible to produce acetamide with high selectivity. The separation of acetamide (T<sub>boil</sub> = 221 °C, T<sub>fusion</sub> = 82.3 °C) from water is simple. In the second reactor on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> promoted by acid one should carry out the acetamide dehydration to acetonitrile. The above-mentioned methods lead to: 1) the decrease of expenses on rectification of acetonitrile; 2) to reduce considerably formation of the compaction products, and to extend the catalyst life between regeneration; 3) to reduce of amount of circulating ammonia; 4) to increase the productivity on acetonitrile from unit of volume of the catalyst.

#### References

- Lida S., Togo H. Direct oxidative conversion of alcohols and amines to nitriles with molecular iodine and DIH in aq NH<sub>3</sub>. *Tetrahedron* 2007; **63**: 34-8274.
- Pavlov O.S., Karsakov S.A., Pavlov S.Yu. Development of processes for C4 hydrocarbons separation and 1,3-butadiene purification. *Theoretical Foundations of chemical Engineering* 2011; **45**: 6-858.
- Henke H. *Liquid chromatography*. M.: «Technosfera»; 2009.
- Brazdil J.F. Acrylonitrile. *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim: Wiley-VCH; 2005. doi:10.1002/14356007.a01\_177.pub3
- Galanov S.I., Kurina L.N., Sidorova O.I., Golovko A.K. Catalytic synthesis of acetonitrile by ammonolysis of acetic acid. *Petroleum Chemistry* 2003; **43**: 4-283.
- Hou Xue-Mei, Yan Li, Zhang Xin, Li Yan-Wei, Li Chuan-Bi Synthesis of Acetonitrile Catalyzed by Solid Acid SO<sub>4</sub>-/ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. *Jilin Normal University Journal (Natural Science Edition)* 2009; **30**: 2-108.

7. Cheng Feng, Yuecheng Zhang, Yining Zhang, Yanlong Wen, Jiquan Zhao. Study on alumina-supported cobalt–nickel oxide catalyst for synthesis of acetonitrile from ethanol. *Catalysis Letters* 2011; **141**: 168.
8. Hu Y., Cao J., Deng J., Cui B., Tan M., Li J., Zhang H. Synthesis of acetonitrile from ethanol via reductive amination over Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. *Reaction Kinetics, Mechanisms and Catalysis* 2012; **106**: 127.
9. Galanov S.I., Sidorova O.I., Golovko A.K., Philimonov V.D., Kurina L.N., Rozhdestvenskiy E.A. Catalytic synthesis of acetonitrile by ammonolysis of acetic acid. *Eurasian ChemTech Journal* 2001; 3-173.
10. Tanabe K. *Catalysts and catalytical processes*. M.: «Mir»; 1993
11. Galanov S.I., Sidorova O.I., Kurina L.N., Golovko A.K. Catalytic synthesis of acetonitrile. *Catalysis in Industry* 2004; 4-27.
12. Gas phase thermochemistry data [Thermodynamics Research Center (TRC) NIST/TRC Table Database]: <http://webbook.nist.gov/cccbdb>, free.