Catalytic Synthesis of Acetonitrile by Ammonolysis of Acetic Acid

S.I. Galanov[*1,2], O.I. Sidorova[*2], A.K.Golovko[2], V.D. Philimonov[3],

L.N. Kurina[1,2], E.A. Rozhdestvenskiy[1]

[1]Tomsk State University, 36, Lenina Ave., 634050, Tomsk, Russia
[2]Institute of Petroleum Chemistry, 3, Academichesky Ave., 634021,Tomsk, Russia
[3]Tomsk Polytechnical University, 30, Lenina Ave., 634043, Tomsk, Russia

Abstract

The influence of principal parameters (reagent ratio, reaction temperature, temperature gradients along a catalyst layer) on the yield of the desired product was studied in the reaction of acetonitrile synthesis from acetic acid over γ-alumina. Thus, the increase in ammonia:acetic acid ratio leads to the increase in acetonitrile selectivity and yield. In this work it has been demonstrated that initial temperatures of 360-380°C are optimum to effectively carry out the process of acetonitrile synthesis. The increase in reaction temperature allows one to increase the yield of acetonitrile, but at elevated temperatures the catalyst carbidization and contamination of the desired product were observed. The additives to the reaction mixture of the substances that decrease the rate of compaction products (CP) formation and participate in the desired product formation are very effective for decreasing the catalyst carbidization. The effect of the composition of a reaction mixture on a catalyst lifetime is considered. The addition of ethyl acetate to acetic acid promotes a greater carbidization as compared to pure acetic acid. The application of a mixture of acetic acid with acetic anhydride at similar acetonitrile yield decreases the catalyst carbidization.

Introduction

Acetonitrile is widely used in organic synthesis as an intermediate reagent, solvent, azeotropizer [1,2]. Acetonitrile is commercially produced as a by-product of acrylonitrile synthesis. Therefore the investigation and development of inexpensive and commercially convenient methods for acetonitrile production represent an urgent problem. Developed are the methods for acetonitrile synthesis from ammonia and acetic acid [3,4], alcohols [5], paraffins and olefins [1,6]. Nevertheless, the syntheses from alcohols [5], paraffins and olefins [1,6] are characterized by an insufficient selectivity and low process efficiency.

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 with space velocity of acid feed of 0.3 h^{-1} [3] and 0.0076-0.06 mol/s·l [4], acetonitrile yield above 80 % was observed at the temperatures of 440-480°C. But the reaction carried out at this temperatures, along with high energy expenses for reactor heating, leads to thermal pyrolysis of acid (or products of synthesis) followed by catalyst carbidization and contamination of the desired product. At elevated temperatures, when steel reactors are used, hydrocyanic acid may be formed. The reduction of the temperature of the synthetic process up to 350-380°C is promising because it is possible to use water steam to heat the reactor instead of flue gases [4].

Thus, the optimization of acetonitrile synthesis should be carried out by the following parameters:
- Enhancement of acetonitrile efficiency per a unit of catalyst volume;
- Reduction of the amount of intermediate products (ammonia acetate and acetamide) and by-products that determine the energy expenses for rectification and purification of acetonitrile;
- Reduction of the reactor temperature that determines the energy expenses of the production and the period of the catalyst life between regenerations.

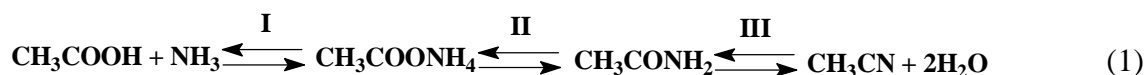*corresponding authors. E-mail: galanov@xf.tsu.tomsk.su

Experimental

The study was made in a flow steel (12X18H10T) reactor with an upward reagent flow at a preheating of the reaction mixture up to the reaction temperature. To enable the temperature measurements in the catalyst layer, the reactor was made with an internal thermocouple pin with moving platinum - platino-rhodium (PP) thermocouple passing through the catalyst layer; thermal EMF was measured by a volt-meter. To reduce coaxial temperature gradients, the reactor was placed into a heated massive unit made of steel [7], the unit temperature was regulated by a high-precision temperature controller (BPT-3) with a PP thermocouple; the precision of the temperature maintenance was 0.5°C. The initial temperature in the reactor (metal unit) was regulated by a BPT-3 temperature controller. During blank tests the temperature gradient was 6-8°C along the 185-mm high catalyst layer with the graining of 1-2 mm. The temperature difference between the external reactor wall and the middle of the layer was 0.5-1.0°C. NH_3:CH_3COOH ratio was changed within 1.5-4.0, the reaction temperature was 350-450°C, acetic acid load was 0.49-1.02 $g/cm^3 \cdot h$. 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 catalyst was γ-Al_2O_3 (S_{spec} = 149 m^2/g, total pore volume is 0.68 cm^3/g). The synthesized products (H_2O, NH_3, CH_3COONH_4, CH_3CN, CH_3CONH_2, CH_3COCH_3, CH_2O and HCN) were analyzed by gas chromatography on a column 3 mm in diameter, 2 m long, SDA Separon as a sorbent, the detector was a catarometer, carrier gas was helium.

Results and discussion

The reaction of acetonitrile formation from acetic acid and ammonia occurs at several stages [3, 4]:

$$CH_3COOH + NH_3 \underset{\underset{I}{\longrightarrow}}{\longleftarrow} CH_3COONH_4 \underset{\underset{II}{\longrightarrow}}{\longleftarrow} CH_3CONH_2 \underset{\underset{III}{\longrightarrow}}{\longleftarrow} CH_3CN + 2H_2O \qquad (1)$$

The reaction of acetamide formation is weakly exothermal: ΔH= –25.3 κJ/mol, the next stage III of acetonitrile formation is endothermal: ΔH = 127.9 κJ/mol [8]. Endothermal process is stable under all the circumstances (in distinction to exothermal one), that is why at a constant heat exchange only one stationary state takes place. Temperature drop leads to the decrease in reaction rate that stops the further temperature reduction, in the similar way the system turns back into its original state at the temperature rise. That is why at the establishment of a stationary reaction mode the temperature gradients (temperature reduction) are observed along the catalyst layer (see Fig. 1). The shape and distribution of temperature gradients along the catalyst layer may be one of the parameters to control the reactor operation. In this case the heat balance of the reactor is described by the following equation:

$$Y_f w \frac{dT}{dz} = h_i r_i - q \qquad (2)$$

where Y_f is the heat capacity of the volume unit, J/$m^3 \cdot K$; w is the linear rate of the flow, m/s; h_i is the thermochemical factor, J/kg; r_i is the reaction rate, $kg/m^3 \cdot s$; $q = \frac{4\alpha}{d}(T_C - T)$ is the heat amount input to a unit of the reaction volume per a time unit in a reactor with the constant temperature of the metal unit T_c; T is the temperature in the reactor; d is the diameter of the pipe containing a catalyst; α is an effective factor of heat transfer from the heat-transfer agent to the catalyst.

The changes in the temperature profiles along the catalyst layer shown in Figure and the data given in Table 1 allow determining an optimum acetic acid load (contact time) at the temperature of 360°C (Fig. 1 b, c). The conversion and selectivity reached the maximum values when the temperature gradients in the final section of the catalyst layer are not observed (Fig. 1, Table 1). This evidences a complete reaction process. The reduction in the acid load (increase in contact time) from 1.02 to 0.58-0.67 $g/cm^3 \cdot h$ at the increase of acetonitrile yield (Table 1) leads to a decrease in efficiency from 0.57 to 0.4-0.46 g of acetonitrile per cm^3 of a catalyst·hour, in this case a side reaction of acetic acid decomposition is observed followed by acetone formation. The acetone selectivity is 0.6 % at the acid load of 0.58 g/cm^3 (Table 1). At the acid load of 1.02 $g/cm^3 \cdot h$ and the temperature of
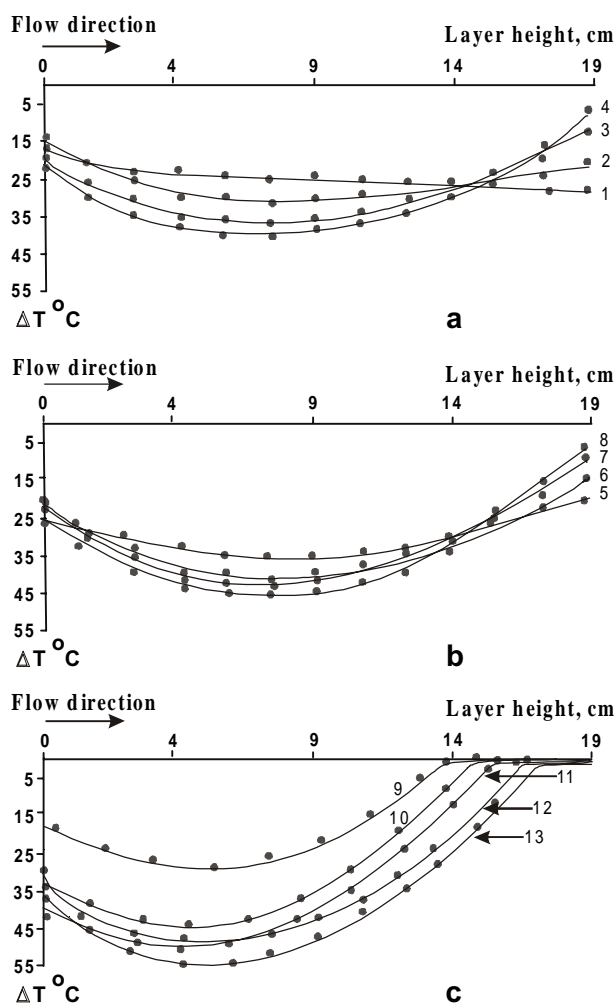
Fig. 1. Profiles of the temperature drop along the catalyst layer. a, b: the initial reactor temperatures are 350 and 360°C, respectively, acid load is 1.02 g/cm³·h; c: for the curves 9, 10, 11 the initial reactor temperature is 360°C, acid loads are respectively 0.49, 0.58, 0.67 g/cm³·h; for the curves 12 and 13 the initial reactor temperature is 380°C, acid load is 1.02 g/cm³·h.

350-380°C acetone is not detected in the reaction products.

One of the parameters influencing the process of acetic acid ammonolysis may be varying the partial pressures of the reactants. The study of the influence of $NH_3:CH_3COOH$ ratio on the process parameters demonstrated that at equal acid loads the increase in ratio leads to the increase in acetonitrile selectivity and yield despite of the reduction in contact time (Table 1). This is connected to the reversibility of the reaction II (Eq.(1)), the increase in the partial pressure of ammonia shifts the equilibrium towards acetamide formation followed by acetonitrile formation (reaction III). The decrease in acetonitrile yield at the dilution of acetic acid by water was noted elsewhere

[3, 4], in this case water influences the equilibrium shift both on the stage II and III. Based on the dependence of temperature gradients (temperature decrease) along the catalyst layer for low ammonia:acid ratio of 1.5 and 2.0 and $T_{in} = 350°C$ (Fig. 1a) one may see that due to the reversibility of the reaction II the temperature gradient along the catalyst layer is minimum, the yield of the desired product (acetonitrile) is low. On increase in partial ammonia pressure (Fig. 1a) the temperature gradient at the final section of the catalyst layer decreases, at the increased yield of the desired product (Table 1). The increase in initial temperature in the reactor by 10°C provokes the increase in temperature gradients in the middle of the catalyst layer (Fig. 1 a, b) at the increase in acetonitrile selectivity and yield (Table 1). This effect may be explained by the increase in the rate of the reaction III (Eq. (1)) and the shift of the equilibrium of the reaction II towards acetamide formation. On increase in acid load and ammonia:acid ratio (enhancement of the space velocity of reactants, reduction in contact time), at a comparable acetonitrile yield (experiment № 8 as compared to experiments № 9, 10, 11) a temperature drop by 10°C is observed in the final section of the catalyst layer, connected with a large mass transfer and cooling of the catalyst layer by the reagent flow. The rise in initial temperature of the reactor from 360 to 380°C at the same acid load significantly accelerates the stage III (Diagram 1) and leads to the increase in the absolute value of the temperature gradient from $\Delta T = 25\text{-}35°C$ ($T_{layer} = 325°C$) to $\Delta T = 45\text{-}55°C$ ($T_{layer} = 325°C$). Correspondingly, (Fig. 1b, curves № 5-8, and c, curves № 12, 13), maximum temperature drop occurs in the initial section of the layer. Temperature gradients are not observed in the final section. Thus, the increase in selectivity and yield of acetonitrile may be reached by increasing the reaction temperature (Table 1).

In addition to energy expenses for reactor heating, the temperature selection is conditioned by cracking processes: the contamination of the desired product by the products of thermal pyrolysis and catalyst carbidization followed by the reduction in catalyst activity. Thus, due to catalyst carbidization, at T = 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 CP formed (Table 2) and to extend the catalyst life between regenerations. The maximum carbidization of catalyst in the initial section of the

Table 1

Influence of the reactant ratio, acetic acid load and temperature on process parameters
(*- temperature gradients of experiments show in Figure, with corresponding numbers)

*No of experiment	T_{in}, °C	Q, g/cm^3·h	NH$_3$:CH$_3$COOH ratio	τ_{rec}, s	K, %	$S_{CH_3CONH_2}$, %	S_{CH_3CN}, %	B_{CH_3CN}, %
1	350	1.02	1.5	1.75	88.5	37.8	62.2	55.1
2	350	1.02	2.0	1.50	92.1	25.4	74.6	68.7
3	350	1.02	3.0	1.10	92.0	13.9	86.1	79.2
4	350	1.02	4.0	0.89	92.2	10.8	89.2	82.2
5	360	1.02	1.5	1.75	88.6	13.4	86.6	76.7
6	360	1.02	2.0	1.50	89.6	11.2	88.8	79.5
7	360	1.02	3.0	1.10	92.9	6.6	93.4	86.8
8	360	1.02	4.0	0.89	100	3.9	96.1	96.1
9	360	0.49	2.0	3.13	100	-	99.3	99.4
10	360	0.58	2.0	2.68	99.2	-	99.4	98.7
11	360	0.67	2.0	2.30	99.2	-	99.5	98.5
12	380	1.02	1.5	1.75	99.5	4.5	95.5	95.0
13	380	1.02	2.0	1.5	99.5	3.0	97.0	97.0

τ_{red} is the reduced contact time at the reaction temperature, s
Q is the acetic acid load, g/cm^3·h
K - acetic acid conversion, %
$S_{CH_3CONH_2}$, S_{CH_3CN} is respectively acetamide and acetonitrile selectivities (mol %)
B_{CH_3CN} is acetonitrile yield (mol %)

Table 2

Influence of the temperature and reaction mixture composition on the formation of compaction products (CP), changes
in specific surface and average catalyst efficiencies per hour of a sample (initial specific surface $S_{spec}=149.0$ m^2/g)

No	T_{in}, °C	Reaction mixture composition	% CP	S_{spec}, m^2/g	$\bar{a}_{cat}$
1	400-460	CH$_3$COOH	0.14	133	0.532
2	350-400	CH$_3$COOH	0.04	141	0.575
3	350-400	95 wt.% CH$_3$COOH + 5 wt.% (CH$_3$CO)$_2$O	0.02	138	0.623
4	350-400	95 wt.% CH$_3$COOH + 5 wt.% CH$_3$COOC$_2$H$_5$	0.73	120	0.226

% CP is the percentage of the compaction products formed per catalyst weight per 1 cm^3 of the acid input.
$\bar{a}_{cat}$ is the average catalyst efficiencies per hour, g of acetonitrile per cm^3 of catalyst·h

catalyst layer downstream of the reaction mixture flow was observed, the final section of the layer being carbided the least and the last. Probably, it is connected with the accumulation of water formed in the reaction gases and with the decrease in the concentration of acetic acid, the main CP source. Hydrogen-carbon analysis of the carbided samples demonstrated that C:H ratio in compaction products is ~2. Hydrogen and carbon make only 30-40 % of the compaction products formed (their content is 8-10 % of catalyst weight), the rest consists, obviously, of oxygen and nitrogen. One of the methods for decreasing the catalyst carbidization is the introduction of water vapours to the reaction mixture, nevertheless, as noted in [3, 4], the application of diluted acetic acid results in the reduction in acetonitrile yield and catalyst efficiency. That is why justified is adding to the reaction mixture of the substances that would decrease the rate

of CP formation and participate in the reaction that results in the formation of the desired product, e.g., acetamide, ethylacetate or acetic anhydride. The addition of ethyl acetate to acetic acid promotes a greater carbidization (Table 2) as compared to pure acetic acid. The application of a mixture of acetic acid with 5 wt % of acetic anhydride at similar acetonitrile yield decreases the catalyst carbidization (Tables 2, 3).

When using an acid-anhydride mixture, an increase in the conversion is observed but acetonitrile yield remains the same as at pure acetic acid application due to the decrease in acetonitrile selectivity (Tables 1, 3). This is connected with the fact that at the introduction of acetic anhydride into the reaction mixture, along with the reactions shown in Eq.(1), the reactions of the acetic anhydride are added:
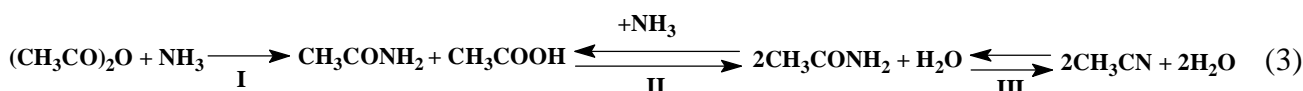
$$(CH_3CO)_2O + NH_3 \xrightarrow{\quad I \quad} CH_3CONH_2 + CH_3COOH \underset{II}{\overset{+NH_3}{\rightleftharpoons}} 2CH_3CONH_2 + H_2O \underset{III}{\rightleftharpoons} 2CH_3CN + 2H_2O \quad (3)$$

Table 3
Influence of the ratio of reagents and temperature on the catalytic parameters of process.
Space velocity of mixture - 1.02 h^{-1} (95 wt.% CH$_3$COOH and 5 wt.% (CH$_3$CO)$_2$O)

No	T_{in},°C	NH$_3$:CH$_3$COOH ratio	K, %	$S_{CH_3CONH_2}$, %	S_{CH_3CN}, %	B_{CH_3CN}, %
1	360	1.5	92.5	16.2	83.8	77.5
2	360	2.0	95.0	12.6	87.2	82.8
3	380	1.5	98.2	4.1	95.7	93.9
4	380	2.0	99.5	3.7	96.3	95.8

Conclusions

Thus, to effectively carry out the process of acetonitrile synthesis, NH$_3$:CH$_3$COOH ratio of 2-3 and initial temperatures of 360-380°C are optimum (application of a mixture of acetic acid with acetic anhydride). At the beginning the rise in the initial reactor temperature to 440°C allows one to improve the acetonitrile efficiency by 30 % (as compared to the initial temperature of 380°C) from 0.680 to 0.886 g of acetonitrile per cm^3 of catalyst·h, then due to the catalyst carbidization it decreases. Under these conditions the average efficiency is 0.806 g of acetonitrile per cm^3 of catalyst·h. In this case the life between regenerations of a catalyst operated at $T_{in} = 440$°C reduces, as compared to the time of operation at $T_{in} = 380$°C. Regeneration time, taking into account a smooth temperature rise and a stepwise increase in oxygen content in oxygen-vapour mixtures intended to prevent catalyst overheating and destruction, is 2 hours. The reduction of the reaction temperature and addition of acetic anhydride to acetic acid enables to increase average catalyst efficiencies per hour $\bar{a}_{cat}$ (Table 2) calculated using Eq.(4) due to the absence of resinous compounds formed at a high-temperature pyrolysis of acid in the reaction products, that allows one to extend the installation operation without catalyst reloading, as the regeneration significantly provokes the catalyst destruction.

$$\bar{a}_{cat} = (a_{cat}·\tau_1)/(\tau_1+\tau_2) \quad (4)$$

where a_{cat} is the efficiency of an active catalyst; τ_1, τ_2 are respectively the duration of the periods of activity and activity recovery [9].

References

1. Paushkin Ya.M, Osipova L.V. Uspekhi Khimii.1959. Vol. XXVIII, n 3. p. 237-263.
2. Pereushanu V., Korobya M., Muska G. Production and Application of Hydrocarbons.// Transl. from Romanian. V.G. Lipovich, G.L.Avrekh (Ed). Moscow: Khimiya. 1987. p. 288.
3. Kovalenko T.I., Kovalenko V.I., Malook G.P., Dubchenko V.N. Zhournal Prikladnoy Khimii. 1972. N 8. P. 1824-1827.
4. Khcheyan Kh.E., Shatalova A.N., Nikitin A.K. Improvement of the Processes of Main Organic Synthesis: in Book of Scientific Papers of VNIIOS . M., TSNIITEneftekhim, 1984. p. 24-31.

5. Vodolazhskiy S.V., Yakushkin M.I., Devekki A.V., Khvorov A.P. Zhournal Organicheskoy Khimii. 1988. Vol. 24 N 4. P. 699.
6. USSR Patent N 738657, MPC B 01 J 23/24. Aliyev S.M., Sokolovskiy V.D., Boreskov G.K.
7. Ioffe I.I., Pismen L.M. Engineering Chemistry of Heterogeneous Catalyst. Moscow, Khimiya. 1965. 246 p.

8. Rabinovich V.A., Khavich Z.Ya. Brief Chemical Handbook. Moscow, Khimiya. 1978. 392 p.
9. Khaylov V.S., Brandt B.B. Introduction in the Technology of Main Organic Synthesis. Moscow, Khimiya. 1969. 560 p.