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MACROKINETIC AND KINETIC REGULARITIES OF CYANIDATION REACTION OF HIGHER ALIPHATIC ALCOHOLS

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ABSTRACT
It was studied the macromolecular and kinetic study of high molecular alcohols of the reaction of cyanide with ammonia on the CHM-1 catayst. In order of to study the macromolecular dependence of nitrile production yield on the rate of gas stream and the diameter of the catalyst. The partial pressures of reactants and products also found to affect to the rate of the reaction.

KEYWORDS: Macrokinetics, kinetics, alcohol, nitrile, mechanism, partial pressure, the rate of the reaction.

I.   INTRODUCTION
Nitriles and amines are the most important products of basic organic and petrochemical synthesis and are used in many branches of the national economy. In connection with the constant expansion of application sphere and scope of the use of nitrogen-containing organic compounds, the researches aimed at creating new high efficient methods of obtaining them are becoming increasingly important. This paper is devoted to the study of macrokinetic and kinetic regularities of the cyanidation reaction of higher aliphatic alcohols using the example of pentadecyl alcohol with ammonia in the presence of the industrial catalyst CHM-1. When heterogeneous reactions take place on solid catalysts, the transfer effects associated with transport of mass and heat are of great importance [1]. The influence of these factors becomes noticeable and even decisive when the reaction rate proves to be comparable with or less than the transfer process speed. In this connection, in studying the kinetic regularities, it is necessary first to carry out the experiments aimed at eliminating or minimizing the effects associated with the transport of starting materials from a number of gas streams to the outer and inner surfaces of the catalyst pellets.

II.   MATERIALS AND METHODS
An analysis of the available literature data makes it possible to conclude that up to now no information has been published in the literature on the influence of the linear velocity and the size of the catalyst pellets on the cyanidation process of higher aliphatic alcohols. This circumstance, as well as the application of CHM-1 catalyst in the study, does not even allow us to roughly estimate the boundaries of these factors that ensure the course of reactions in kinetic region. Thereby, it seemed necessary to conduct a detailed study of the influence of the linear velocity of gas stream and the size of the catalyst grain on proceeding regularities of the cyanidation process. The study was carried out using the example of cyanidation of pentadecyl alcohol at a total pressure of 0.1 MPa, partial pressures of the alcohol 0.014 MPa and ammonia 0,086 MPa in temperature range of 230-270ºC. The influence of the linear velocity of the initial mixture on the kinetics of the reaction was studied in the interval 1.3-5.2 cm/sec at a specific rate of the initial alcohol feed of 23.0 and 35.3 mol/kg.cat.h. The linear velocity was varied by changing the amount of the alcohol-ammonia mixture fed into the reaction. The constancy of the specific rate of the alcohol feed was achieved by the corresponding change in the catalyst charge. The obtained results in studying the influence of the linear velocity of the gas stream on conversion degree of alcohol to nitrile showed that in this temperature range and specific rates of alcohol feed, an increase in the linear velocity of the gas stream from 1.3 to 2.5 cm/sec is accompanied by a noticeable increase in conversion degree of the initial alcohol to nitrile. Further increase in the linear velocity does not have a significant effect on the yield of the nitrile. Consequently, in the range of linear velocities from 1.3 to 2.5

cm/sec, the kinetics of the reaction studied was complicated by the transport of reactants to the outer surface of the catalyst pellets. At linear rates of gas flow 2.5 cm/sec and higher external diffusion inhibition is not observed.

III.   RESULTS AND DISCUSSION

To study the influence of the catalyst grain size on the cyanidation of pentadecyl alcohol, the experiments were performed with a change in grinding degree of the catalyst particles from 0.5-1.0 to 2-3 mm. The results are shown in Table 1.

Table 1. The influence of the size values of the catalyst grain on the conversion degree of pentadecyl alcohol to nitrile (T=250°C, linear velocity of gas flow 5.0 cm/sec)

Specific rate of alcohol feed, mol/kg.cat.h.	Size of the catalyst grain, mm	Degree of alcohol conversion,%	Degree of alcohol conversion	
			to nitrile	to by products
23,0	0,5-1	66,0	63,5	2,5
23,0	1-2	65,5	62,5	3,0
23,0	2-3	66,0	62,5	3,5
35,3	0,5-1	50,0	47,5	2,5
35,3	1-2	49,0	46,0	3,0
35,3	2-3	48,0	46,0	2,0

It can be seen from the data in Table 1 that the change in the size values of the catalyst grain in the studied range does not appear to be the degree of conversion of the alcohol to nitrile. This circumstance indicates the absence in the studied conditions of a significant influence of the transfer of the reacting substances inside the catalyst pellets on the kinetics of the reaction studied.

Heterogeneous catalytic processes, both on a laboratory and on an industrial scale, are increasingly being carried out in flow systems. This is due to the need for more use of reactive devices in modern technology, which is possible only in continuous flowing systems.

When studying kinetic regularities in a flow system, carrying out the reaction to deep degrees of transformation of the starting materials leads to the appearance of a concentration gradient along the catalyst layer. In this case, the kinetic equation will be expressed in integral form.

Haugen and Watson [2] proposed to work with a very thin layer of catalyst, while passing along which the degree of transformation of the starting materials, and consequently the composition of the gas mixture, varies little. The main advantage of conducting research at low degrees of conversion of reagents is that it allows to calculate the process speed directly from the experimental data. Therefore, when processing the experimental results, it does not have to resort to integrating the differential form of the kinetic equation. Since the data on the speed of the process in a differential form are obtained under conditions of practical absence of gradients of concentration and temperature, they acquire the dignity of physicochemical constants at a given degree of conversion.

In connection with the foregoing, a series of experiments was carried out to study the dependence of the conversion degree of pentadecyl alcohol to nitrile on its inverse specific feed rate under conditions that providing the reaction in the kinetic region in the temperature range 230-270°C with an interval of 20°C.

The investigations were carried out in a flowing glass reactor with an inner diameter of 8 mm in the presence of a CHM-1 catalyst (grain size 1-1.5 mm). The experiments were carried out at a comparatively high linear velocity of the gas mixture (18.5 cm/sec) with dilution of the catalyst (1:1) with an inert packing (quartz glass of the same grain size). Such a procedure for carrying out the experiments (as shown by a direct measurement of the temperature in the reaction zone) made it possible to carry out the cyanidation reaction under conditions close to isothermal. The obtained experimental data are presented in Table 2.

Table 2. Results on the study of the influence of the specific rate of alcohol feed on the process of its cyanidation at different temperatures (Partial pressure of the alcohol 0.014 MPa, ammonia 0.078 MPa, helium 0.08 MPa)

Specific rate of alcohol feed, mol/kg.cat.h.	Temperature of synthesis, ºC	Conversion degree of alcohol to nitrile, %	Formation speed of nitrile, mol/kg.cat.h.
396	230	-	-
306	230	3,5	11,4
197	230	6,0	13,0
143	230	7,5	12,2
110	230	9,0	11,7
396	250	6,0	25,0
306	250	7,0	22,8
197	250	10,5	22,9
143	250	14,0	22,8
396	270	9,0	37,4
306	270	11,5	37,5
197	270	17,5	38,0

The linear dependence obtained in this series of the experiments in the coordinates $\frac{1}{V} - x$ over the entire studied range of specific rates of alcohol feed (110-396 mol/kg.cat.h.) and temperatures (230-270ºC) shows that under these conditions a flow differential reactor is realized.

For a detailed study of the kinetics and mechanism of cyanidation reaction of pentadecyl alcohol with ammonia, the effect of the partial pressures of the initial and final products on the reaction rate has been studied by changing the partial pressure of one component (P_i) at constant partial pressures of others. The invariability of the linear velocity of the initial mixture was provided by introducing helium into the reaction zone if necessary. The constancy of the specific rate of alcohol feed in varying its partial pressure was achieved by changing the catalyst charge appropriately. In this case the specific rate of alcohol feed was from 110 to 396 mol/kg.cat.h., which provided, in the chosen temperature range, the realization of the differential reactor. The experiments were carried out at the values of the linear velocity of the gas flow and the size of the catalyst grain, which provide the reaction proceeding in the kinetic region.

The results obtained in the study of the effect of alcohol partial pressure on the process of its cyanidation at different temperatures and at constant linear velocity of the gas stream are presented in Table 3.

Table 3. Results on the effect of alcohol partial pressure on the process of its cyanidation with ammonia at various specific rates of feed and temperatures
(Total pressure 0.1, partial pressure of ammonia 0.078 MPa).

$Y_{alcohol}$, mol/kg.cat.h.	$P_{alcohol}$, MPa	Conversion degree of alcohol to nitrile, %			Formation speed of nitrile, mol/kg,cat,h.		
		T=230ºC	T=250ºC	T=270ºC	T=230ºC	T=250ºC	T=270ºC
396	0.007	-	6.5	10.0	-	28.0	42.0
306	0.007	4.5	9.0	12.5	14.7	29.3	40.8
197	0.007	6.5	12.5	-	14.1	27.1	-
143	0.007	9.5	-	-	15.5	-	-

110	0.007	11.0	-	-	14.3	-	-
396	0.014	-	6.0	9.0	-	25.0	37.4
306	0.014	3.5	7.0	11.4	11.4	22.8	37.5
197	0.014	6.0	10.5	17.0	13.0	22.9	38.0
143	0.014	7.5	14.0	-	12.2	22.8	-
396	0.019	-	4.5	7.5	-	18.6	31.2
306	0.019	-	6.0	10.0	-	19.6	32.6
197	0.019	4.5	8.0	14.5	9.8	20.6	31.5
143	0.019	6.0	11.5	-	9.8	18.8	-
110	0.019	8.0	-	-	10.4	-	-

As follows from the experimental data, an increase in alcohol partial pressure from 0.007 to 0.019 MPa leads to a decrease in the degree of its conversion into nitrile in the entire studied range of temperatures and specific rates of feed.

In connection with the obtained data, it seemed necessary to study the effect of the partial pressure of the initial alcohol on the degree of its conversion in a wider range at a constant specific rate of the feed. This cycle of investigations was carried out in the interval of alcohol partial pressure 0.002-0.009 MPa in the temperature range 230-250°C.

It has been experimentally established that the dependence of the conversion degree of the initial pentadecyl alcohol on its partial pressure at a constant specific rate of the feed has the form of a curve with a maximum. Such kinetic regularities are characteristic for the mechanism involving the interaction of at least two adsorbed particles or involving at least two active sites on the catalyst surface.

The effect of the partial pressure of ammonia on conversion degree of alcohol to nitrile was studied in the range 0.030-0.078 MPa. Regulation of the partial pressure of ammonia was achieved by changing the rate of its feed to the reaction zone. The rate of alcohol feed to the catalyst was maintained unchanged. The constancy of gas flow velocity in it was achieved by introducing the necessary amount of helium into the reaction zone.

The experiments have shown that the change in the partial pressure of ammonia under the studied conditions does not affect the conversion of pentadecyl alcohol to nitrile. For example, at a temperature of 250°C and a specific rate of alcohol feed 143 mol/kg.cat.h. an increase in the partial pressure of ammonia from 0.030 MPa to 1.78 MPa did not lead to the increase of conversion degree of alcohol to nitrile - 12.5% and 13.0%, respectively.

To obtain more complete information on the kinetics of the process studied, it seems necessary to investigate the effect of the reaction products on the rate of cyanidation of pentadecyl alcohol. This series of the experiments was carried out at a partial pressure of alcohol 0.007 MPa, ammonia 0.078 MPa.

On the basis of the experimental data, it was established that a change in the concentrations of ammonia, nitrile and hydrogen does not affect the degree of conversion of alcohol to nitrile, but water greatly reduces the rate of its cyanidation.

Analyzing the literature data on studying the kinetic laws of cyanidation of aliphatic and aromatic alcohols [3-5] and the obtained results in studying the effect of the partial pressures of the reagents and the reaction products on cyanidation process of pentadecyl alcohol in the presence of CHM-1 catalyst, one can note the presence of general laws: with the increase of the partial pressure of alcohol, the rate of nitrile formation decreases throughout the entire studied range of parameters change, at the same time, the dependence of the conversion degree of the alcohol on its partial pressure at a constant specific rate of the feed has the form of a curve with a maximum. It should also be noted that ammonia, hydrogen and nitrile do not influence the conversion degree of the alcohol to nitrile in the studied partial pressure range, but water significantly reduces the rate of its cyanidation. Based on this, it can be assumed that, despite the differences in the structure of the initial alcohol, and also the composition of the catalyst, the formation mechanism of higher aliphatic nitriles from the appropriate alcohols and ammonia is identical to the previously identified formation mechanism of aliphatic nitriles [3]. Then the principal stage diagram of the formation of higher aliphatic nitriles in accordance with [3] can be represented as follows:

1. $RCH_2OH + Z \Leftrightarrow RCH_2OH\ Z$
2. $NH_3 + Z \Leftrightarrow NH_3\ Z$
3. $RCH_2OH\ Z + Z \Leftrightarrow RCHO\ Z + H_2\ Z$
4. $RCHO\ Z + NH_3\ Z \Leftrightarrow RCH = NH\ Z + H_2O\ Z$

5. $RCH = NH\ Z + \Leftrightarrow RCN\ Z + H_2\ Z$
6. $RCN\ Z \Leftrightarrow RCN + Z$
7. $H_2O\ Z \Leftrightarrow H_2O + Z$
8. $H_2\ Z \Leftrightarrow H_2 + Z$

where, Z - the active center of the catalyst.

As before, the scheme provides for the dehydrogenation of the starting alcohol with the participation of two active catalyst centers (stage 3) as a limiting step. In view of this circumstance, the rate will be determined by the rate of the direct reaction of the third stage:

$$W = W_3 = K_3 Q_{RCH_2OH} Q_o$$

where, K_3 - the constant of the direct reaction of the third stage, MPa^{-1}, Q_{RCH_2OH} - the proportion of the surface occupied by alcohol, Q_o - the proportion of free surface.

From the conditions of dynamic equilibrium of the remaining stages we obtain:

$$W = \frac{K_3 K_{RCH_2OH} P_{RCH_2OH}}{(1 + K_{RCH_2OH} P_{RCH_2OH} + K_{NH_3} P_{NH_3} \frac{K_{RCN} K_{H_2O} K_{H_2}}{K_5 K_4 K_{NH_3}} \frac{P_{RCN} P_{H_2O} P_{H_2}}{P_{NH_3}} + \frac{K_{RCN} K_{H_2}}{K_5} P_{RCN} P_{H_2} + K_{RCN} P_{RCN} + K_{H_2O} P_{H_2O} + K_{H_2} P_{H_2})^2}$$

where, K_4 and K_5 - the constants of the corresponding stages, $K_{RCH_2OH}, K_{NH_3}, K_{H_2O}, K_{RCN}, K_{H_2}$ - the adsorption coefficients of alcohol, ammonia, water, nitrile and hydrogen, $P_{RCH_2OH}, P_{NH_3}, P_{H_2O}, P_{RCN}, P_{H_2}$ - the partial pressure of alcohol, ammonia, water, nitrile and hydrogen.

It can be seen from the above scheme that the surface concentration of the aldehyde must be extremely small due to slow stage of its formation (stage 3) and its rapid conversion on stage 4. This circumstance makes it possible to eliminate from the kinetic equation the term corresponding to the aldehyde.

Taking also into account that ammonia, nitrile and hydrogen do not influence the kinetics of the process, equation (1) can be written as follows:

$$W = \frac{KK_{RCH_2OH} P_{RCH_2OH}}{(1 + K_{RCH_2OH} P_{RCH_2OH} + K_{H_2O} P_{H_2O})^2} \qquad (2)$$

Thus, equation (2) describes the kinetic regularities of the cyanidation process of higher aliphatic alcohols in the presence of industrial CHM-1 catalyst.

IV.   CONCLUSION
1. The kinetic regularities of the reaction of catalytic cyanidation of pentadecyl alcohol with ammonia have been studied in the temperature range from 230 to 270OC and in a wide range of partial pressures of the reactants and reaction products.
2. It has been established that with increasing alcohol partial pressure the rate of nitrile formation decreases in the entire studied range of parameter changes, while the dependence of the degree of alcohol transformation on its partial pressure at a constant specific feed rate has the form of a curve with a maximum.
3. It has been found out that ammonia, hydrogen and nitrile do not influence the degree of conversion of alcohol to nitrile in the studied partial pressure range, and water significantly reduces the rate of its cyanidation.
4. On the basis of the data obtained, the kinetic equations describing the regularities of the cyanidation of higher aliphatic alcohols in the presence of the industrial CHM-1 catalyst are derived.

V.   ACKNOWLEDGEMENTS

VI.   REFERENCES

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