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KINETICS OF PYRROLE FORMATION FROM ACETYLENE, AMMONIA AND AMINES

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Abstract. The research findings of the pyrrole formation from acetylene, ammonia and amines varying catalysts and reaction conditions have been studied in the work. The cadmium catalysts developed by us selectively lead to pyrrole formation using aluminum fluoride as a promoter. The change in the rate of acetylene consumption depending on the weight of the catalyst according to the Boreskov criterion shows that external diffusion does not influence under the conditions of $T=573\text{K}$ and $P_{(C_2H_2)} = 0.1\text{ atm}$. The values of the rate of acetylene consumption of at 4, 2, 1, 0.5 mm sizes of catalyst grains with similar conditions, internal diffusion does not influence on the observed rate of acetylene consumption. Calculation on the Thiele modulus shows that the reaction of acetylene consumption does not experience intra-diffusion inhibition. The presence of a noticeable amount of macropores in the porous catalyst grain eliminates the appearance of a temperature gradient and causes a high kinetic ability of the reaction.

Keywords: pyrrole, acetylene, ammonia, amines, catalyst, dehydration, heterocyclization

Introduction. The modern level of advanced technology development contributes to innovative research in the field of heterocyclic compound chemistry - pyrrole and its derivatives.

Pyrrole derivatives are widely used in various sectors of the economy.

Many of them have high physiological activity and, at the same time, the pyrrole structure is vital for compounds such as chlorophyll and hemoglobin, which play a key role in the basic metabolism processes of [1, 2].

Among the known methods for synthetic pyrrole production, the authors have achieved certain successes in the catalytic interaction of acetylene, ammonia and amines, which production have been established in Uzbekistan.

By varying the catalysts and reaction conditions (at temperatures of 320–340°C), it was possible to increase the pyrrole yield up to 12.4% [3, 4].

In order to develop a technology for the synthetic pyrrole production, kinetics and mechanism of pyrrole formation from acetylene and ammonia at least with 98.5 and 99.0% purity, respectively, has been studied [5].

Experimental part. The experiments were carried out on a gradientless reactor. The weight of the catalyst was 1–20 g., the effective grain diameter varied in the range of 0.5–4 mm. The conversion degree of acetylene was 10–80%. The delivery rate of the source gases was controlled by means of rheometers, the flow rate after the reactor was measured by a film flow meter and a rheometer. The use of rheometers with various capillaries made it possible to measure the volumetric flow rate of acetylene in the range 0.002 - 5.0 l / g, ammonia 0.5 - 10.0 l / g, while the deviations of the set values did not exceed 2 ÷ 5 %.

Developed by the authors, cadmium catalysts form the selective pyrrole formation process. It has been experimentally established that when aluminum fluoride is used as a promoter, the stability of the latter increases sharply.

The structure of π - complexes of acetylene and ammonia with divalent cadmium salts should be affected by the composition of active centers on the catalyst surface [6].

It is similarly polarized on cadmium and ammonia hydroxy fluorides.



The active particles formed in the above-mentioned processes react generating vinylamine, which in association with acetylene generates divinylamine and cyclizes to pyrrole [7].

Results and discussion. Preliminary experiments showed that the rate of acetylene consumption and pyrrole formation is directly proportional to the weight of the catalyst (using KFCA (cadmium-fluorine-zinc-chromium-aluminum)).

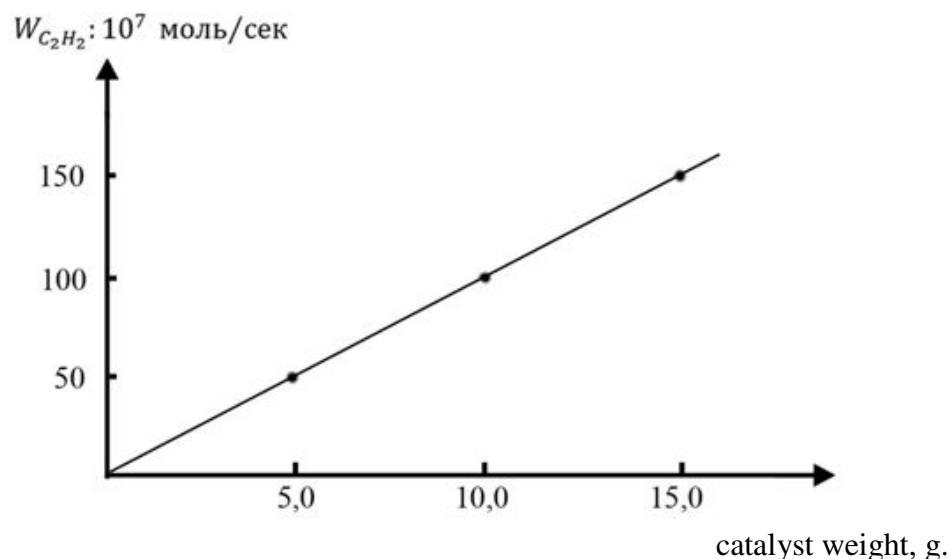


Fig. 1: Change in acetylene flow rate depending on the catalyst weight (Synthesis conditions: $T = 573 \text{ K}$; $P_{C_2H_2} = 0,1 \text{ atm}$)

This allows us to conclude that the mass transfer from the catalyst surface simulates the speed of the process and thus, the reaction does not meet externally - diffusion limitations.

The possibility of the external diffusion influence can also be estimated using the Boreskov criterion:

$$\Delta C \frac{2,32 * \Gamma_{C_2H_2} * d_p}{D_{C_2H_2} * S_v * Re_b^{0,7} * P_r^{0,3}} ; \quad (1)$$

where $G_{C_2H_2}$ is the rate of the chemical reaction of the consumption of acetylene;

d_p - catalyst grain diameter;

$D_{C_2H_2}$ - diffusion coefficient of acetylene in ammonia;

S_v - the outer surface of the catalyst grain, referred to the volume of grain;

Pr - 3600 * M is the Prandtl number;

$Re_b = 4$ is the Reynolds number according to Boreskov;

C is the difference in the concentration of acetylene between the gas stream and the surface of the catalyst; if $\Delta C * 100\% < 1\%$, then the influence of external diffusion can be neglected.

Substituting in the formula (1) the specific parameter values at T-600K, we obtain:

$$P_{C_2H_2} = 0,1 \text{ atm} ; \quad \Gamma_{C_2H_2} = 10^{-6} \text{ моль/см}^3 \cdot \text{с} ; \quad d_p = 10^{-1} \text{ см} ;$$

$$D_{C_2H_2} = 2 \cdot 10^{-4} \text{ с/см} ; \quad S_v = 40 \text{ см}^{-1}$$

$$Pr_{0,3} = 7,94 ; \quad Re^{0,7} = 36,8$$

$$\mu_{NH_3} = 2 \cdot 10^{-4} \text{ с/см} ; \quad U = 2,5 \cdot 10^3 \text{ см/с}$$

$$E = 0,4 ; \quad P_{NH_3} = 3,45 \cdot 10^{-4} \text{ с/см}$$

We get $\frac{\partial C}{C} = 5 \cdot 10^{-4}$

The calculation shows that the influence of external diffusion can be neglected [8]:

U - is the linear flow rate;

E - is the porosity of the catalyst;

ρ - is the density of ammonia;

μ - ammonia viscosity;

To clarify the possible effect of internal diffusion on the process rate, we have studied the dependence of the acetylene consumption rate on the effective diameter of the catalyst grain. The values of the consumption rate of acetylene for various grain sizes of the catalyst:

$$T = 573 \text{ K} ; \quad P_{C_2H_2} = 0,1 \text{ atm} ; \quad P_{NH_3} = 0,9 \text{ atm} ;$$

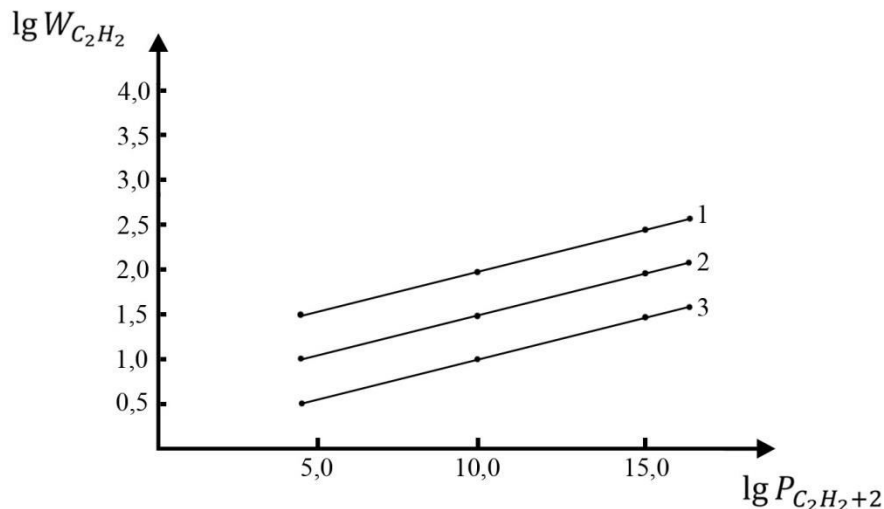


Fig. 2: Change in the logarithm of the specific rate of acetylene consumption depending on the logarithm of the partial pressure of acetylene.

$$W_{C_2H_2} [\text{mol/g cat. sec.}] ; P_{C_2H_2}$$

Synthesis conditions,

1-573K ; 2-523K ; 3-473K

$W_{C_2H_2} * 1 \text{ mol/g. cat. sec.}$	8,4	8,2	8,6	8,5
$d_{grain} \text{ мм}$	4	2	1	0,5

The data presented indicate that internal diffusion does not affect the observed rate of acetylene consumption.

The influence of internal diffusion can also be estimated by means of Thiele modulus:

$$\Psi = L \cdot \sqrt{\frac{K}{D \cdot E}} = L \sqrt{\frac{W_{C_2H_2}}{D_{C_2H_2} \cdot \Gamma \cdot [C_{C_2H_2}]}}; \quad (2)$$

Where

L is the determining grain size;

G is the radius of the transport pores;

Ψ - Thiele module.

When calculating the parameter Ψ , it was assumed that the first substance inside the grain passes through transport pores by means of molecular pores which radius $Gr = 103\text{\AA}$ is comparable with the mean free path of acetylene molecules at atmospheric pressure. This assumption is valid if there is a noticeable amount of macropores in the porous catalyst grain, i.e. for bidispersed catalysts, which include alumina, which is the carrier of the active components in the KFCA catalyst.

$$T = 573 \text{ K} ; P_{C_2H_2} = 0,5 \text{ атм} ; W_{C_2H_2} = 10^{-3} \text{ моль/м}^2 \cdot \text{сек.}; \\ D_{C_2H_2} = 5 \cdot 10^{-5} \text{ м}^2/\text{сек}$$

$$\Gamma = 2 \cdot 10^{-7} ; Z = 4 \text{ мм}$$

$$\Psi = 4 \cdot 10^{-3} \sqrt{\frac{10^{-3}}{5 \cdot 10^{-5} \cdot 2 \cdot 10^{-7} \cdot 10}} = 0,04 < 1; \quad (3)$$

An approximate calculation indicates that the acetylene consumption reaction does not experience intra-diffusion inhibition.

If a temperature gradient occurs during the reaction inside the grain, this can have a complex effect on the observed values of the speed and activation energy. To clarify the conditions for the occurrence of temperature gradients inside the grain, we used the heat balance equation for an individual grain under stationary conditions:

$$W_{C_2H_2} \Delta H q_{kat} = \lambda \cdot \frac{dT}{dt}; \quad (4)$$

Where

$W_{C_2H_2}$ - acetylene decomposition rate;

ΔH - thermal effect of the reaction J/mol;

q_{kat} - catalyst grain weight, g .;

λ - coefficient of thermal conductivity;

J/sm. Sec. grad.;

Integrating Equation and Substituting Velocities $W_{C_2H_2} 10^{-7}$ моль/г. cat. sec. (under 573K, $P_{C_2H_2} = 0,3$ атм, heat effect $\Delta H = 4 \cdot 10^5$ J/mol, grain mass $d_{кат} = 4,7 \cdot 10^{-7}$ г.,

We get:

$$T_k = T_s + \frac{10^{-7} \cdot 4 \cdot 10^5 \cdot 4,7 \cdot 10^{-2} \cdot 2 \cdot 10^{-1}}{8 \cdot 10^{-3}} = 1 + \frac{T_s}{0K}; \quad (5)$$

Where

T_s - temperature on the surface of the grain, K;

T_k - temperature inside the grain, K.

An approximate calculation shows that under the conditions of study of the kinetics reaction, the temperature gradient inside the grain can be neglected.

Conclusion. Thus, the kinetics of pyrrole formation from acetylene and ammonia has been studied. The cadmium catalysts developed by us from a selective pyrrole formation process using aluminum fluoride as a promoter. The presented data indicate that internal diffusion does not affect the observed acetylene consumption rate. The effect of the catalyst composition including the carriers, the reaction temperature, the volumetric rate, and the ratio of the starting reagents on the pyrrole yield has been studied. An approximate calculation indicates that the acetylene consumption reaction does not experience intradiffusion inhibition. It is shown that the rate of acetylene consumption is not affected by internal and external diffusion of acetylene.

Reference

1. Chemical Encyclopedia, Moscow. g. 1995. Volume 4. p. 1078-1080.
2. T.K. Inakov, N. Madikhanov, A.G. Makhsumov. "Synthesis of pyrrole homologues." // Academy of Sciences of the Uzbek SSR. Uzbek chemical journal. No. 1, 1976.
3. S. M. Turabjanov, R. A. Tashkaraev. "Promoted catalysts in liquid-phase organic synthesis technology" // Chemistry and Chemical Technology. Tashkent 2011. No 3. p. 14-29.
4. D. Yusupov, K. M. Akhmerov. "Catalytic heterocyclization of acetylene compounds" // Tashkent. Fan. 1985.S. 180.
5. S.M. Turabjanov, Sh.P. Nurullaev, Man Hu. "Kinetics of natural gas purification processes with composite absorbents" // Jiujiang Petroleum & Chemical Factory No. 4. 2013. p. 20-25.
6. Boreskov G.K. "Catalysts and catalytic processes" // Novosibirsk 1977. with 2-56.
7. U. Shokirov, S. Turabjanov, H. Kadirov, L. Rakhimova. "Development of one-stage methods for the catalytic process for the preparation of pyrrole and its derivatives" // Uzbek Chemical Journal.-2019. No. 2. p. 73-77.
8. Flid R.M. "Kinetics and mechanism of catalytic transformations of acetylene. On some questions of the reaction mechanism of the attachment of various molecules to acetylene" // Journal of Organic Chemistry 1958.v 32-No.10 p.2339-2346.

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