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A Novel Vanadium Catalyst for Oxidation of Hydrogen Chloride with Dioxygen

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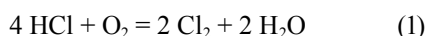
A novel catalytic system for oxidation of hydrogen chloride, V₂O₅-LiCl-KCl, has been studied. This catalyst shows activity in a range of relatively low temperatures, 250 – 350 °C. Chlorine yield attains 200 – 780 g per kg of catalyst per hour at 350 °C, which greatly exceeds the characteristics of known vanadium, copper and chromia catalysts.

Keywords: hydrogen chloride, oxidation, chlorine, oxygen, vanadium, catalyst.

1. Introduction

Chlorine is a principal reactant used in chlorine metallurgy and industrial production of chlororganic compounds. An important problem associated with these processes is regeneration of molecular chlorine by oxidation of hydrogen chloride, a principal byproduct of such industries [1,2]. An attractive solution to this problem is oxidation of hydrogen chloride with dioxygen because energy cost of this process can be as low as 15 % of that required by electrolysis [1].

The possibility of catalytic oxidation of hydrogen chloride with dioxygen



in the presence of copper(II) chloride at 350 – 450 °C was first discovered by Deacon in 1868. Low productivity (chlorine yield approx. 10-20 g per kg of catalyst per hour) and low conversion at temperatures above 400 °C make this process

unsuitable for industrial applications. Numerous attempts to improve performance of copper-based catalysts led to the increase of chlorine yield to 50 g / (kg catalyst · hr) at 350 °C [3]. Also, a two-stage process was developed, with the catalyst oxidation and reduction stages carried out in separate reactors, which allows to achieve almost 100 % hydrogen chloride conversion [4].

In ca. 1980-90 spinel catalysts based on chromium(III) oxide were actively studied. The copper-chromium catalyst produces 80 – 90 g of chlorine per liter of catalyst per hour at 350 °C. The cobalt-chromium catalyst allows to achieve the chlorine yield of 150 and 250 g / (l catalyst · hr) at 350 and 425 °C, respectively. Cobalt-chromium catalysts are also described as being more stable under reaction conditions than copper catalysts [5]. Numerous patents [6-8] describe greater productivity of chromia catalysts with chlorine output approx. 600 g / (kg catalyst · hr).

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Several patents of the recent decade [9-10] describe highly productive ruthenium(IV) oxide catalysts with chlorine yield up to 2 - 3 kg / (kg catalyst · hr). The structure of RuO₂/TiO₂ catalysts, mechanism of catalytic reaction, and pilot plant for the corresponding catalytic process are described in [1,11,12], however, data on kinetics of such process are not presented.

A work by Benson [13] discusses thermodynamics of catalysts for Deacon process and a possibility of using vanadium(V) oxide for this purpose. However, experiments with vanadium catalyst resulted in its quick evaporation.

A patent [14] describes the use of V₂O₅ in molten mixture of sulfates and pyrosulfates of alkaline metals as a catalyst for oxidation of hydrogen chloride with dioxygen. With this catalyst, the chlorine output is approx. 20 g / (kg catalyst · hr) at 375 – 400 °C.

Behavior of systems comprising V₂O₅ and chlorides of alkaline metals, over the temperature range 300 – 450 °C, is studied in [15]. Such systems release chlorine at these temperatures, and V⁺⁴ is oxidized back to V⁺⁵ in the presence of dioxygen. The weight loss rate of such systems increases markedly when a system gets molten. These facts indicate the possibility of using the described systems as catalysts for the Deacon reaction.

The goal of the present paper is to study the catalytic activity of the low-melting system V₂O₅-LiCl-KCl towards hydrogen chloride oxidation with dioxygen.

2. Experimental

“Chemically pure” and “pure for analysis” grade chemicals were used in the present work. A dry mixture consisting of 71.1 wt.% V₂O₅, 13.2 % LiCl, and 15.7 % KCl was used to synthesize the catalyst. This mixture corresponds to eutectic LiCl-KCl composition

(melting point 352 °C [16]) and molar ratio vanadium - chloride of 3 : 2. This mixture was calcined at 380 °C for three hours. The resulting sintered mass was crushed and, after sieving fractionation, was used as the catalyst in hereinafter described experiments.

The installation used for HCl oxidation consists of series-connected high-pressure cylinder with oxidant gas (air or oxygen), a water-sealed gas meter (Trommelgaszahler-NB 0.75, Junkalor, Germany), a bubbler saturator used for saturating the gas mixture with hydrogen chloride, a U-shaped glass reactor installed in a gradientless electric furnace, and a system of valves.

A sample of catalyst, supported between layers of glass wool, is loaded into one of the U-shaped glass reactors (i.d. 7 mm or 21 mm, heated inner empty volume between the catalyst bed and exit from reactor is 7 and 65 cm³, respectively). Initial gas mixture containing required HCl concentration was obtained by bubbling oxidant gas through 34 % hydrochloric acid contained in the thermostat-controlled bubbler saturator. Hereinafter provided gas flow rate values indicate the rate of gas flow through the reactor which is calculated from oxidant gas flow rate values (measured by the gas meter) considering the volume occupied by HCl added to the flow in the saturator.

The reacted gas mixture, upon leaving the reactor, is fed into a bubbler tube containing 10 % solution of KI. Upon completion of an experiment, the solution in this tube undergoes standard analytical titration with Na₂S₂O₃ solution to determine the I₂ content, and with NaOH solution to determine the amount of unreacted HCl.

X-ray diffraction (XRD) analyzes of powder samples were performed in 2θ angles range from 5° to 70° using DRON-3 diffractometer (LOMO, Russia) in scanning mode. Step of scanning used was 0.02° with point, acquisition time used

was 1 s. Cu K α 1 radiation was used with Ni-monochromator. Individual crystalline phases were identified from observed XRD patterns using the *JCPDS* database [17].

3. Results and discussion

Table 1 shows experimental data on oxidation of hydrogen chloride with air on the studied catalyst in the temperature range 250 – 275 °C. The chlorine yield attains 6 – 29 g / (kg catalyst · hr) at 250 °C, and 15 – 48 g / (kg catalyst · hr) at 275 °C. Highest of these values exceed the performance of known copper catalysts at the temperature of 350 °C and higher [3].

Oxidation rate increases approximately two-fold when temperature is risen by 25 °C. Rise of gas flow rate causes oxidation rate increase. These facts suggest that kinetics of the process are diffusion controlled.

With increase of the catalyst mass, the chlorine yield increases as well, but not proportionally: total chlorine formation rate rises by a factor 1.85 – 2.6 with a three-fold catalyst mass increase. Conversion of hydrogen chloride under given conditions does not exceed 2 %. Hence, alteration of gas phase composition due to occurring reaction is insignificant, and this can not explain the decrease of reaction rate per unit catalyst mass with increase of catalyst amount in the reactor. We believe that this result indicates that the reaction occurs not only on the catalyst surface but also in the gas phase. In order to confirm this assumption, we carried out several experiments in the reactor of greater internal diameter. Considering the volume occupied by the catalyst, the free heated volume of this latter reactor is 13 times greater than that of the former reactor. Such increase of the gas phase heated

Table 1. Low temperature oxidation of hydrogen chloride on the V₂O₅-LiCl-KCl catalyst (grain size 0.2 - 0.63 mm). Hydrogen chloride content in mixture with air – 15 vol.%, (saturator temperature 32 °C). Reaction duration 30 min

| Reactor temperature, °C | Reactor i.d., mm | Catalyst mass, g | Gas mixture flow rate, l/hr | Amount of chlorine formed, mmol-eq | Chlorine yield, g / (kg catalyst · hr) |
|-------------------------|------------------|------------------|-----------------------------|------------------------------------|--|
| 250 | 7 | 1 | 4.2 | 0.14 | 9.94 |
| 250 | 7 | 1 | 8.5 | 0.20 | 14.2 |
| 250 | 7 | 2 | 4.2 | 0.17 | 6.04 |
| 250 | 7 | 2 | 8.5 | 0.27 | 9.59 |
| 250 | 7 | 3 | 4.2 | 0.26 | 6.15 |
| 250 | 7 | 3 | 8.5 | 0.52 | 12.3 |
| 275 | 7 | 1 | 4.2 | 0.29 | 20.6 |
| 275 | 7 | 1 | 8.5 | 0.39 | 27.7 |
| 275 | 7 | 2 | 4.2 | 0.42 | 14.9 |
| 275 | 7 | 2 | 8.5 | 0.64 | 22.7 |
| 275 | 7 | 3 | 4.2 | 0.69 | 16.3 |
| 275 | 7 | 3 | 8.5 | 0.90 | 21.3 |
| 250 | 21 | 1 | 4.2 | 0.30 | 22 |
| 250 | 21 | 1 | 8.5 | 0.41 | 29 |
| 275 | 21 | 1 | 4.2 | 0.49 | 35 |
| 275 | 21 | 1 | 8.5 | 0.70 | 48 |

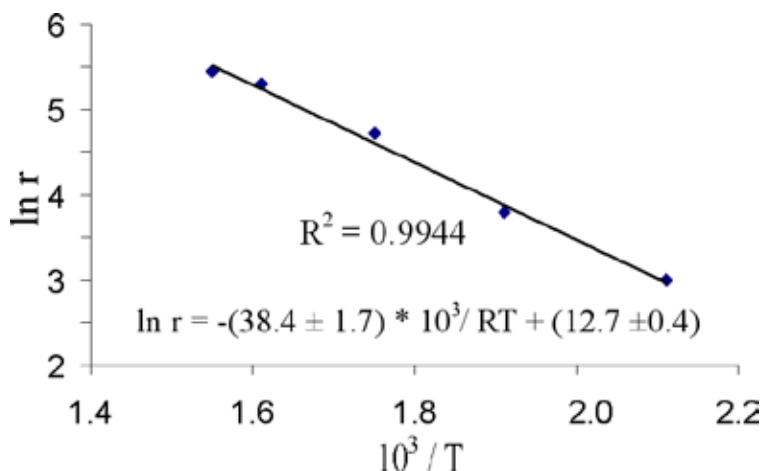


Fig. 1. Dependence of chlorine yield versus temperature, in Arrhenius coordinates (for reaction conditions see Table 2)

volume results in 1.7 – 2.3 times increase of chlorine yield. Since the reaction does not occur in the absence of catalyst, this result suggests that a catalyzed gas-phase pathway of the reaction takes place. The gas-phase reaction is probably catalyzed by vanadyl chloride, a volatile product of interaction between hydrogen chloride or chloride ion of the catalyst and the solid catalyst. Compared to rate of the heterogeneous catalytic reaction, rate of the gas-phase oxidation per unit of reactor volume is relatively low (approximately 10 - 20 times less).

Fig. 1 demonstrates the dependence of catalytic oxidation rate versus temperature, in Arrhenius coordinates. The temperature rise from 200 to 370 °C leads to increase of the chlorine yield from 20 to 233 g / (kg catalyst · hr). The apparent activation energy is 38.4 ± 1.7 kJ/mol, and this value confirms the conclusion on diffusion controlled nature of kinetics of the process [18].

Data of Table 2 show increase of hydrogen chloride conversion and decrease of chlorine yield per unit catalyst mass with rise of catalyst amount at 350 °C. The decrease of chlorine yield per unit mass of the catalyst may be determined by two reasons. The first

is decrease of the reactants concentration as a result of conversion increase, and the second is oxidation in the gas phase catalyzed by VOCl_3 , as discussed above.

To further increase the reaction rate, the dioxygen and HCl concentrations were increased from 20 and 20 vol. % to 62 and 35 vol. %, correspondingly (Table 3). The chlorine yield exceeds 500 g / (kg catalyst · hr) under these conditions. The obtained results exceed the values at low reactants concentration (Table 2, row 1) by a factor of 2.75, at the catalyst mass of 1 g. Also, this value exceeds the activity of the cobalt-chromium and copper-chromium catalysts at 350 °C by 1.6 and 3 times, respectively [5]. At the catalyst mass of 5 g, the chlorine yield attains 180 – 210 g / (kg catalyst · hr), and the HCl conversion is in the range of 30 – 36 %.

To estimate stability of the catalyst, experiments 2 – 5 were consequently carried out with the same catalyst sample without its replacement or regeneration. The catalytic activity slightly decreases (4 – 15 %) during the studied period of two hours together with the loss of the catalyst mass (2.6 wt. % per hour). In case of lower catalyst mass, 1 g, it loses weight as fast as 10 % per hour.

Table 2. Oxidation of hydrogen chloride with air at 350 °C. Catalyst grain size 0.63 - 1 mm. Reactor i.d. 7 mm. Gas mixture flow rate 6.3 l/hr (linear velocity 4.5 cm/s), HCl content 20 vol.%, (saturator temperature 41 °C). Reaction duration 30 min

| Catalyst mass, g | Amount of chlorine formed, mmol-eq | Chlorine yield, g / (kg catalyst · hr) | Catalyst mass decrease, mg | HCl conversion, % |
|------------------|------------------------------------|--|----------------------------|-------------------|
| 1 | 2.7 | 191.7 | 70 | 4.8 |
| 2 | 4.48 | 159.0 | 130 | 8 |
| 3 | 6.21 | 147.0 | 140 | 11.1 |

Table 3. Stability of the catalyst for oxidation of hydrogen chloride with dioxygen at 350 °C. Reactor i.d. 21 mm. Gas mixture flow rate 7.7 l/hr (linear velocity 0.6 cm/s). Catalyst grain size 1 - 1.6 mm. Catalyst mass 5 g. HCl content in gas mixture 35 vol.% (saturator temperature 50 °C)

| №№ | Reaction duration, min | Amount of chlorine formed, mmol-eq | HCl conversion, % | Chlorine yield, g / (kg catalyst · hr) | Catalyst mass decrease per run, mg. |
|----|------------------------|------------------------------------|-------------------|--|-------------------------------------|
| 1* | 30 | 3.72 | 9 | 528 | 50 |
| 2 | 15 | 6.65 | 33 | 188 | 50 |
| 3 | 15 | 7.40 | 36 | 210 | 70 |
| 4 | 50 | 22.55 | 32 | 192 | 70 |
| 5 | 30 | 12.75 | 30 | 181 | 50 |

Note: experiments 2-5 were consequently carried out with the same catalyst sample.

* Catalyst mass 1 g

Further increase of the reaction rate at 350 °C is attained by raising the gas flow rate (Table 4). The dependence of yield versus flow rate is close to linear, and this also confirms the assumption about diffusion-controlled nature of kinetics of the process. At the flow rate of 25 l/hr (18 cm/s), the chlorine yield attains 777 g / (kg catalyst · hr) which is 2.5 times greater than the productivity of the cobalt-chromium catalyst at 350 °C and is 1.5 times greater than the productivity of said catalyst at 450 °C [5].

Catalyst mass decrease is linearly proportional to gas flow rate (Table 4). This suggests that the decrease of catalyst mass may be determined by either the equilibrium of VOCl_3 formation, or, maybe, diffusion controlled evaporation of VOCl_3 from the catalyst surface.

In all the discussed experiments, atomic ratio of amount of chlorine formed to amount of vanadium(V) initially contained in corresponding

catalyst sample does not exceed 0.71 (row 3 of Table 4). In order to ascertain whether the studied system exhibits the catalytic activity instead of oxygen-independent stoichiometric oxidation of HCl with V^{+5} compounds contained in the catalyst, the experiments without oxygen in the gas flow were carried out. Table 5 contains data on behavior of the $\text{LiCl-KCl-V}_2\text{O}_5$ system when oxidant gas is substituted by argon. Under such conditions, oxidation of HCl with the catalyst's V^{+5} components is going to occur. Compared to the data obtained in the presence of dioxygen (Tables 2-4), the rate of chlorine formation decreases by at least 4 - 5 times after the first 15 minutes of the process. Evidently, this happens as amount of V^{+5} contained in the catalyst decreases due to its reduction. Output of oxygen-independent oxidation is much lower than chlorine yield observed in the presence of dioxygen (Tables 2-4). This clearly proves that the catalytic path of

Table 4. The influence of gas flow rate on the oxidation of HCl with dioxygen at 350 °C. Catalyst mass 1 g, grain size 1-1.6 mm. Reactor i.d. 7 mm. HCl content in gas mixture 20 vol.% (saturator temperature 41 °C). Reaction duration 15 min

| Gas phase flow rate, l/hr (linear velocity, cm/s) | Amount of chlorine formed, mmol-eq | HCl conversion, % | Chlorine yield, g / (kg catalyst · hr) | Catalyst mass decrease per run, mg |
|---|------------------------------------|-------------------|--|------------------------------------|
| 6.3 (4.5) | 1.9 | 19 | 252 | 20 |
| 12.5 (9) | 2.75 | 13 | 391 | 50 |
| 25 (18) | 5.48 | 12 | 777 | 110 |

Table 5. Oxidation of hydrogen chloride with the LiCl-KCl-V₂O₅ system in a current of argon at 350 °C. Reactor i.d. 7 mm. Gas mixture flow rate 6.3 l/hr (4.5 cm/s). Catalyst mass 1 g, grain size 1-1.6 mm. HCl content in gas mixture 20 vol.% (saturator temperature 41 °C)

| Reaction duration, min | Amount of HCl fed into the reactor, mmol | Amount of chlorine formed, mmol-eq | Chlorine yield, g / (kg catalyst · hr) | Catalyst mass decrease per run, mg |
|------------------------|--|------------------------------------|--|------------------------------------|
| 15 | 10.67 | 0.575 | 81 | 30 |
| 30 | 21.57 | 0.675 | 48 | 30 |

Note: two rows of the table represent two consequential runs with the same catalyst sample without its replacement or regeneration.

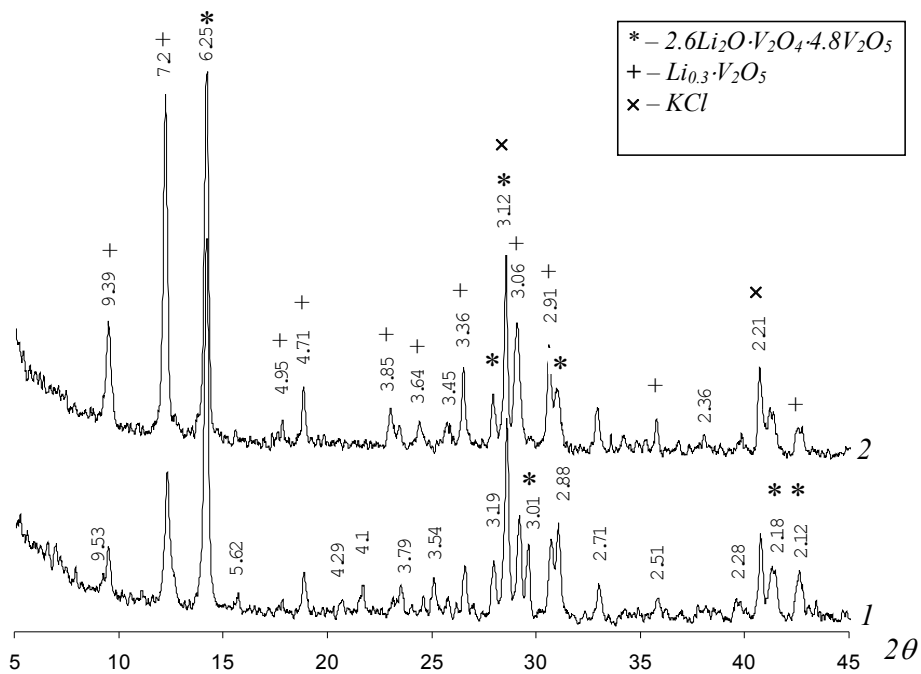


Fig. 2. Fragments of diffractograms of the steady-state (operating in HCl-O₂ flow), and the reduced (operating in HCl-Ar flow with no dioxygen) catalyst samples (fragments 1 and 2, respectively). Interplanar spacings are given in Angstroms

hydrogen chloride oxidation with dioxygen is the main reaction path in the studied system.

Fig. 2 presents fragments of diffractograms of the steady-state (operating in HCl-O₂ flow, for conditions see Table 4), and the reduced (operating in HCl-Ar flow, Table 5) catalyst samples. The steady-state catalyst sample comprises mainly 2.6 Li₂O·V₂O₄·4.8V₂O₅ ($d = 6.25; 3.19; 2.88 \text{ \AA}$ [17]), and a lesser quantity of Li_{0.3}V₂O₅ ($d = 9.39; 7.20; 3.36 \text{ \AA}$ [17]). Intensity of KCl bands ($d = 3.12; 2.21 \text{ \AA}$ [17]) is less than intensity of bands of the main phase.

The reduced catalyst sample contains roughly equal amounts of 2.6Li₂O·V₂O₄·4.8V₂O₅ and Li_{0.3}V₂O₅. KCl content remains at previous level. Both vanadium-containing phases have close vanadium oxidation states (+4.8), but different Li : V ratios: 0.45 for the main phase under the steady-state conditions, and Li : V = 0.15 for the phase which forms when the catalyst is reduced. This means that hydrogen chloride reacts with lithium vanadates with formation of lithium chloride. In the presence of dioxygen this chloride ion may be oxidized with liberation of chlorine.

4. Conclusion

Vanadium catalysts are widely used in the processes of organic substances partial oxidation

at temperatures of 300 °C and higher [18]. We have determined that the vanadium catalyst promoted by the eutectic mixture of lithium and potassium chlorides exhibits catalytic activity towards the reaction of hydrogen chloride oxidation with dioxygen. The chlorine yield attained is as high as 780 g / (kg catalyst · hr) at the relatively low temperature of 350 °C, and the low linear velocity of gas phase flow, 18 cm/s. The activity of the studied catalyst greatly exceeds those of the known copper [3, 4], vanadia-sulphate [14], copper-chromium, and cobalt-chromium systems [5]. The results were obtained under the diffusion-controlled kinetics regime, i.e. are lower estimates, and can be improved by intensification of mass transfer in the oxidation reactor.

Under reaction conditions, the studied vanadium catalyst loses its active component at a rate of approx. 5 % per hour. This is a serious problem, but it is a common problem for practically all known hydrogen chloride oxidation catalysts. There are known catalytic systems that are unstable, but efficiently regenerated in operation cycle, e.g., petrochemicals cracking catalysts [18]. As for the vanadium catalyst discussed, it could be supported, e.g., on silica, and the same support may be used to adsorb vanadium volatile compounds.

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References

1. Iwanaga, K.; Seki, K.; Hibi, T.; Issoo, K.; Suzuta, T.; Nakada, M.; Mori, Y.; Abe, T. The Development of Improved Hydrogen Chloride Oxidation Process. *Sumitomo Kagaku*. 2004, V. 1. P. 4-12.
2. Parfyonov, O. G.; Pashkov, G. L. Problems of Modern Titanium Metallurgy, SB RAS publishing: Novosibirsk (Russia), 2008; 279 p.
3. Engel, W. F.; Wattimena, F. U.S. Patent 3,210,158, 1965.
4. Mortensen, M.; Minet, R. G.; Tsotsis, T. T.; Benson, S. W. The development of a dual fluidized-bed reactor system for the conversion of hydrogen chloride to chlorine. *Chem. Eng. Sci.* 1999. V. 54. P. 2131-2139.

5. Feschenko, L. V.; Vlasenko, V. M.; Chernobrivets, V. L.; Kurilets, Ya. P. Oxidation of hydrogen chloride on cobalt-chromium catalyst. *Journal of Applied Chemistry* (USSR). 1991. V. 64. P. 2040-2044.
6. Itoh, H.; Kono, Yo.; Ajioka, M.; Takenaka, S.; Kataita, M. U.S. Patent 4,774,070, 1988.
7. Ajioka, M.; Takenaka, Sh.; Itoh, H.; Kataita, M.; Kohno, Y. U.S. Patent 5,034,209, 1991.
8. Miyata, K.; Morisaki, J.; Hirayama, T.; Kamachi, H.; Yamada, K. U.S. Patent 5,707,919, 1998.
9. Hibi, T.; Nishida, H.; Abekawa, H. U.S. Patent 5,871,707, 1999.
10. Iwanaga, K.; Yoshii, M.; Suzuta, T. U.S. Patent 6,713,035, 2004.
11. Crihan, D.; Knapp, M.; Zweidinger, S.; Lundgren, E.; Weststrate, C. J.; Andersen, J. N.; Seitsonen, A. P.; Over, H. Stable deacon process for HCl oxidation over RuO₂. *Angew. Chem. Int. Ed.* 2008. V. 47. P. 2131-2135.
12. Zweidinger, S.; Crihan, D.; Knapp, M.; Hofmann, J. P.; Seitsonen, A. P.; Weststrate, C. J.; Lundgren, E.; Andersen, J. N.; Over, H. Reaction Mechanism of the Oxidation of HCl over RuO₂(110) surface. *J. Phys. Chem. C.* 2008. V. 112. P. 9966-9969.
13. Hisham, M. W. M.; Benson, S. W. Thermochemistry of the Deacon Process. *J. Phys. Chem.* **1995**, *99*, 6194-6198.
14. Rohrmann, C. A. U.S. Patent 4,269,817, 1981.
15. Fotiev, A. A.; Slobodin, B. V.; Hodos, M. Ya. Vanadates. Composition, synthesis, structure, properties. Nauka: Moscow (Russia), 1988; 272 p.
16. Massalski, T. B., Editor-in-Chief; Okamoto, H.; Subramanian, P. R.; Kacprzak, L. *Binary Alloy Phase Diagrams - Second edition, 3 vol.*, ASM International: Materials Park, Ohio (USA), 1990.
17. *PDF 2 database*, International Centre for Diffraction Data: Newtown Square, Pennsylvania (USA), 1996.
18. Thomas, C. L. Catalytic processes and proven catalysts. Academic Press: New York and London, 1970; 284 p.