ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

2 (62)

АПРЕЛЬ – ИЮНЬ 2018 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2018

UDC 66.094.37:547.821.411.3:547.826.1

T. P. MIKHAILOVSKAYA, R. KURMAKYZY, D. K. TOLEMISOVA, P. B. VOROBYEV

«A.B. Bekturov Institute of Chemical Sciences» JSC, Almaty, Republic of Kazakhstan

MODIFYING THE INFLUENCE OF TITANIUM AND ZIRCONIUM DIOXIDES ON THE PROPERTIES OF THE VANADIUM OXIDE CATALYST IN THE VAPOR-PHASE OXIDATION OF 3-METHYLPYRIDINE

Abstract. The nature of the modifying effect of titanium- and zirconium dioxide on the properties of the vanadium oxide catalyst in the vapor-phase oxidation of 3-methylpyridine is discussed. It was found that the vanadium oxide catalyst, modified by TiO_2 and ZrO_2 additions, showed the highest activity in the studied process. Nicotinic acid was obtained with the yield of 68% at 270 °C and a molar ratio of 3-methylpyridine:O_2:H_2O = = 1:13:94.

Key words: oxidation, 3-methylpyridine, nicotinic acid, catalysts.

Introduction. Nicotinic acid (NA - niacin, vitamin PP, vitamin B_3) is a vitamin that participates in many oxidative reactions of living cells [1]. Nicotinic acid and its derivatives have a wide variety of physiological properties, due to which they are widely used in medicine and agriculture as vitamins, medicines, plant growth regulators. Nicotinic acid is used to enrich food and animal's feed [2].

Several methods for the preparation of nicotinic acid are known [3]: 1) liquid-phase oxidation: a) oxidation of 3-methylpyridine (3-MP) or β-quinoline with $KMnO_4$ in an alkaline medium. Disadvantages: high expense of expensive $KMnO_4$, the difficulty of implementing continuous technology, the complexity of the scheme for processing queen cells, a large amount of MnO_2 waste, the difficulty of mechanization and automation of the process, the high cost of nicotinic acid; b) oxidation with 30% nitric acid. Disadvantages: high aggressiveness of the environment with the use of HNO_3, which requires the use of expensive corrosion-resistant equipment with special coatings (titanium, cobalt or tantalum), the need for complex absorption systems for nitrogen oxides, complex systems for nitric acid regeneration, a system for cleaning gas emissions, a large amount of waste, acid waste water, a large potential explosion hazard of the process.

Recently, the search for vapor-phase direct oxidation of 3-methylpyridine with air oxygen into nicotinic acid is of special attention. Transition metal oxides are widely used for the preparation of catalysts for the vapor-phase oxidation of methylpyridines. For example, titanium and zirconium oxides are widely used as components of catalytic systems [4-6]. The practical importance of the target product causes interest in finding new effective contacts and studying the effect of oxide additives on the catalytic properties of an oxide-vanadium catalyst.

In this connection, the purpose of this work is to study the effect of titanium dioxide and zirconium dioxide on the catalytic properties of the oxide-vanadium contact in the reaction of vapor-phase oxidation of 3-methylpyridine.

EXPERIMENTAL

In this work used 3-MP, by boiling point 140 °C (692 mm, d_4^{20} = 0.9568, n_D^{20} = 1.5050) which has been dried and distilled. These characteristics corresponded to the reference data.

As initial components of the catalysts, we used vanadium pentoxide, titanium and zirconium dioxides. The initial oxides in a particular ratio were ground in a porcelain mortar to form a homogeneous batch, which was then compressed into tablets of 15 mm in diameter and 3-4 mm in thickness and calcined at 350 and 640 °C for 4 hours. After cooling, the tablets were crushed into grains of 3-5 mm in size.

The oxidation of 3-MP was carried out in a continuous installation of reaction tube made of stainless steel with a diameter of 20 mm and a length of 150 mm into which 9 ml of a granular catalyst was loaded. The unreacted 3-MP and reaction products were trapped in air-lift type scrubbers filled with water and analyzed by gas-liquid chromatography. NA was titrated with 0,035 N alkali using phenolphthalein.

The deep oxidation products were analyzed by LXM-8MD chromatograph with a thermal conductivity detector. The stainless steel columns had a length of 3,5 m and an inner diameter of 3 mm. The adsorbent for CO detection was an AG-5 mk. activated carbon (0,25-0,50 mm), for CO_2 – polysorbent-1 (0,16-0,20 mm). The temperature of the thermostat was 40 °C.

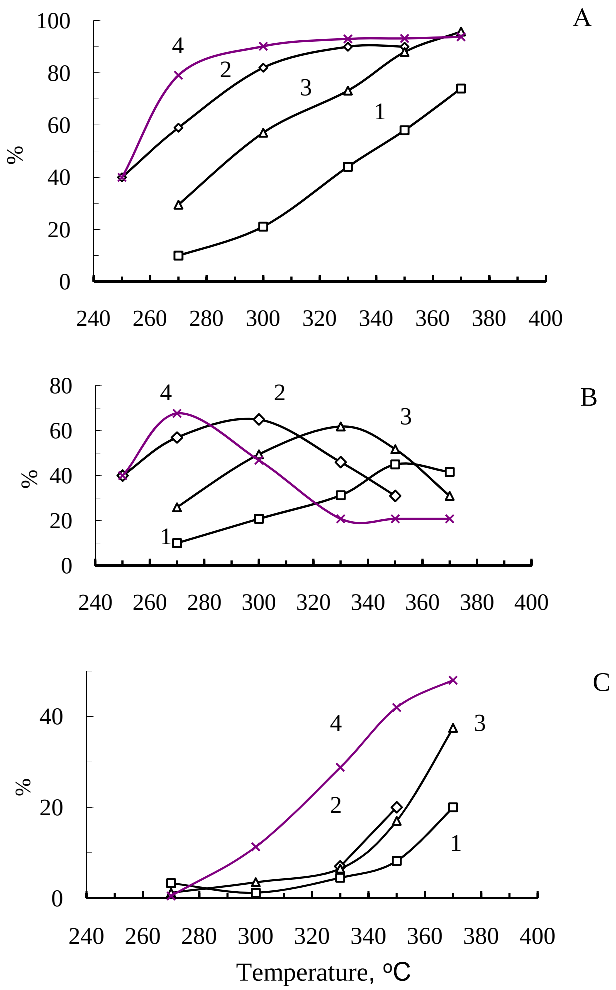
RESULTS AND DISCUSSION

In order to improve the catalytic action of the individual catalyst of vanadium pentoxide in the oxidation of 3-methylpyridine to modify it by adding additives dioxides of titanium and zirconium is of great interest. Binary vanadium-titanium and vanadium-zirconium oxide and three-component vanadium-titanium- zirconium catalysts were prepared and tested.

The general regularities of the reaction, in particular, the effect of temperature, the amount of oxygen (air) fed to the reaction zone and water vapor on the yield of the main reaction products were studied.

The figure shows the results the change in the conversion of 3-methylpyridine and the yield of nicotinic acid (A) on the tested oxide-vanadium catalysts as a function of temperature under comparable conditions. It can be noted that vanadium pentoxide showed the least activity in the oxidation of 3-methylpyridine: the conversion of the starting material even at a temperature of 370 °C was only 70 %. The activity of binary V-Zr-O and V-Ti-O contacts is higher than that of vanadium pentoxide, and the three-component vanadium-titanium-zirconium catalyst of the composition $V_2O_5 \cdot 4TiO_2 \cdot 4ZrO_2$ exhibited the greatest activity.

The main product of oxidation of 3-methylpyridine is nicotinic acid. The figure shows that its yield (B) increases in the following series of oxide-vanadium catalysts: V_2O_5 < V-Zr-O < V-Ti-O< V-Ti-Zr-O. From the presented data, it can



The feed rate of 3-methylpyridine is 36 g, air is 550 l per 1 liter of catalyst per hour.
The molar ratio of 3-methylpyridine:O_2:H_2O = 1:13:94

Effect of temperature on the conversion of 3-methylpyridine (A),
the yield of nicotinic acid (B) and CO_2 (C) under oxidation conditions
on oxide modifying catalyst V_2O_5 (1), V-Ti (2), V-Zr (3), V-Ti-Zr (4)

be seen that the best catalytic properties in the oxidation of 3-methylpyridine exhibited an oxide vanadium-titanium-zirconium catalyst. On this catalyst, when the starting reagents were fed in a molar ratio of 3-methylpyridine: oxygen:woter = = 1:13:94, the conversion of 3-methylpyridine at 270 °C was 80%, and nicotinic acid was obtained with the highest yield about 68 %.

Conclusion. Thus, the conducted tests of modified oxide-vanadium catalysts in the reaction of vapor-phase oxidation of 3-methylpyridine showed that the introduction of titanium and zirconium dioxides contributes to an increase in the activity of the oxide-vanadium catalyst. It has been established that the three-component V-Ti-Zr-O contact directs the oxidation of 3-methylpyridine mainly towards the formation of nicotinic acid: in the low-temperature region (250-270 ^oC) the selectivity of its formation is higher than 85 %.

The research was carried out according to the scientific and technical program No. BR05234667 within the framework of program-targeted financing CS MES RK.

REFERENCES

[1] Komov V.P. Biochemistry. M.: Drofa, 2004. P. 640.
[2] Sarafanova L.A. Food additives: Encyclopedia. 2-nd ed., Rev. and add. St. Petersburg: GIORD, 2004. P. 808. ISBN 5-901065-79-4. (P. 420-221).
[3] Korotchenkova N.V., Samarenko V.Y. Vitamins of the heterocyclic series. Structure, properties, synthesis, chemical technology: Methodological guidelines. St.-Petersburg: Publishing house SPKhFA, 2006. P. 58
[4] Petrov I.Y., Tryasunov B.G. Structure and catalytic properties of deposited oxide-molybdenum, oxide-vanadium and oxide-chromium catalysts for the dehydrogenation of hydrocarbons // Vestn. KuzGTU. 2007. N 3. P. 73-84.
[5] Ibrahim Salem. Recent Studies on the Catalytic Activity of Titanium, Zirconium, and Hafnium Oxides // J. Catal. Rev. Science and Engineering. 2003. Vol. 45, N 2. P. 205-296. doi.org/10.1081/CR-120015740.
[6] Benjaram M. Reddy. Recent Advances on TiO_2-ZrO_2 Mixed Oxides as Catalysts and Catalyst Supports // Catal. Rev. 2005. Vol. 47, N 2. P. 257-296. doi.org/10.1081/CR-200057488.

Резюме

Т. П. Михайловская, Р. Құрмақызы, Д. Қ. Төлемісова, П. Б. Воробьев

3-МЕТИЛПИРИДИНДІ БУ КҮЙІНДЕ ТОТЫҚТЫРУДАҒЫ ВАНАДИЙ ОКСИДТІ КАТАЛИЗАТОРДЫҢ ҚАСИЕТІНЕ ТИТАН ЖӘНЕ ЦИРКОНИЙ ДИОКСИДТЕРІНІҢ МОДИФИЦІРУШІ ӘСЕРІ

3-метилпиридинді бу фазалы тотықтырудағы ванадий оксидті катализатордың қасиетіне титан және цирконий диоксидтерінің әсері талқыланады.

Түйін сөздер: тотығу, 3-метилпиридин, никотин қышқылы, катализаторлар.

Резюме

Т. П. Михайловская, Р. Курмақызы, Д. К. Төлемісова, П. Б. Воробьев

МОДИФИЦИРУЮЩЕЕ ВЛИЯНИЕ ДИОКСИДОВ ТИТАНА И ЦИРКОНИЯ НА СВОЙСТВА ОКСИДНОВАНАДИЕВОГО КАТАЛИЗАТОРА В ПАРОФАЗНОМ ОКИСЛЕНИИ 3-МЕТИЛПИРИДИНА

Обсуждается влияние диоксидов титана и циркония на свойства ванадийоксидного катализатора в парофазном окислении 3-метилпиридина.

Ключевые слова: окисление, 3-метилпиридин, никотиновая кислота, катализаторы.