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CATALYTIC PROPERTIES OF V_2O_5-TiO_2 AND V_2O_5-ZrO_2 BINARY SYSTEMS IN THE VAPOR-PHASE OXIDATION OF 3-METHYLPYRIDINE INTO NICOTINIC ACID

Abstract. The results of catalytic activity of V_2O_5-TiO_2 and V_2O_5-ZrO_2 binary catalysts in the partial oxidation of 3-methylpyridine were investigated. It was found that the V-Ti-O catalyst prepared using highly dispersed titanium dioxide particles (200 nm) and V-Zr-O catalyst significantly exceeds both vanadium pentoxide and TiO_2 (Rutile) based vanadium-titanium contact by its activity. Nicotinic acid is obtained with the yield of 78-80% at 300 °C and a molar ratio of 3-MP:O_2:H_2O = 1:13:94.

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

Introduction. Nicotinic acid (NA) is widely used in medicine as a vitamin PP, a general stimulant for life-supporting processes in the body, a drug that reduces toxic effects, a starting material for the synthesis of cardiac agents such as cordiamine, nicodane, etc., as well as in plant growing as a stimulator for the growth of wheat, cotton, cultures, livestock breeding and, especially, poultry farming.

The vapor-phase oxidation of 3-methylpyridine (3-MP) by air oxygen is the most cost-effective method of nicotinic acid synthesis. In Bekturov Institute of Chemical Sciences, with the purpose of creating a one-stage technological process for the NA production, the research is being conducted for searching the efficient catalysts of 3-MP vapor-phase oxidation.

The vanadium-titanium systems are widely used as catalysts for such an industrially important process as the partial oxidation of hydrocarbons. Titanium dioxide (TiO_2) is one of the components for catalysts of redox processes. Close to titanium dioxide by its chemical properties, zirconium dioxide (ZrO_2) is also widely used in the synthesis of highly selective catalysts, for example, the dehydrogenation of hydrocarbons. The structure and phase composition of oxidized vanadium-titanium and vanadium-zirconium catalysts were studied by Petrov I.Ya. et al. [1] using physicochemical methods (XRD, IR spectroscopy, UV and visible spectroscopy, EPR spectroscopy). It was found that the nature of the TiO_2 supporter has little effect on the structure of the supported vanadium-oxide catalyst. Comparison of samples of V_2O_5-TiO_2 catalysts, based on rutile and anatase, showed that the crystal structure of TiO_2 does not affect the activity of V-Ti-O catalysts in *o*-xylene oxidation [2].

Earlier, we noted the effect of the crystalline modification of TiO_2 on the catalytic properties of V-Ti-O catalysts in the oxidation of 3- and 4-methylpyridines [3]. It was found that V_2O_5-TiO_2 (Anatase) is more active and selective in the formation of pyridine carboxylic acids.

The purpose of this work was to test the new V-Ti-O binary catalyst prepared with highly dispersed titanium dioxide particles (200 nm) and V-Zr-O catalyst in 3-MP oxidation.

Experiment

In this work, dried and distilled 3-MP with boiling point of 140 °/ 692 mm, $d_4^{20} = 0.9568$, $n_D^{20} = 1.5050$ was used. 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 molar ratio of 1:4 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.

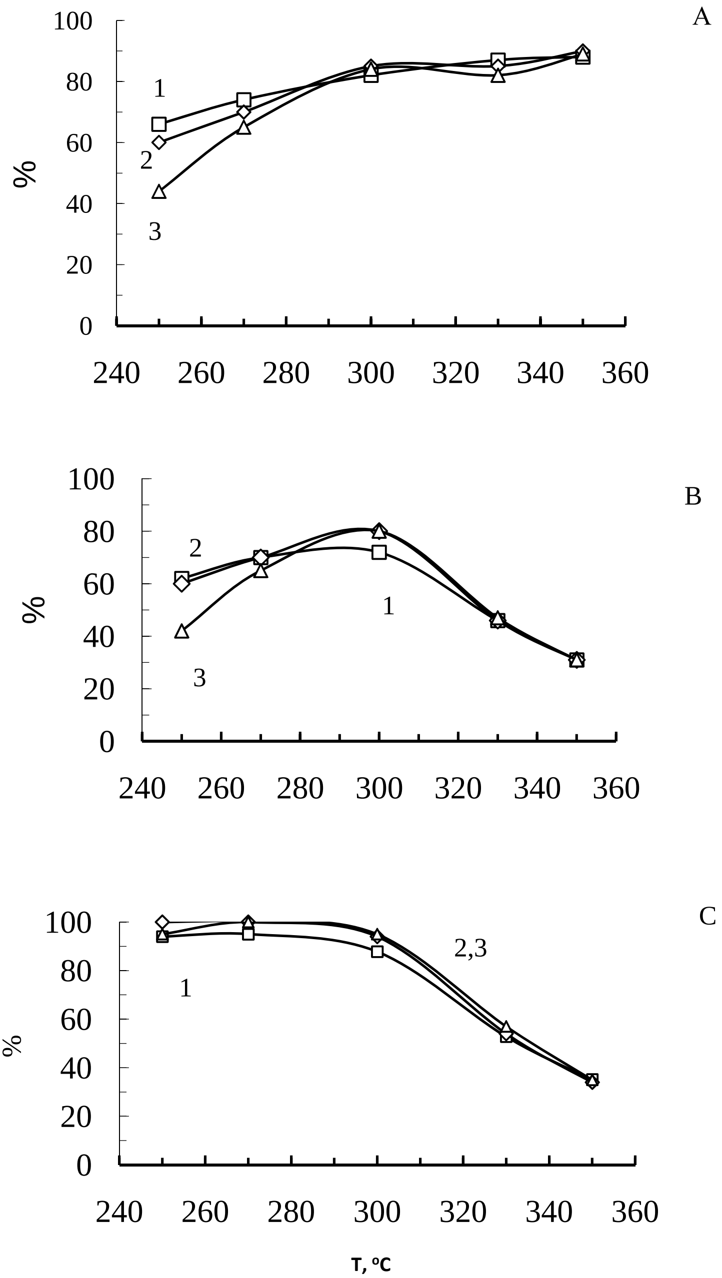
The deep oxidation products were analyzed by LXM-8MD chromatograph with a thermal conductivity detector. The stainless steel columns had a length of 3,5 m and an inner diameter of 3 mm. The adsorbent for CO detection was an AG-5 mk. activated carbon (0,25-0,50 mm), for CO_2 – polysorbent-1 (0,16-0,20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

Results and discussion

The purpose of this article is to compare the catalytic activity and selectivity of V_2O_5-TiO_2 (Anatase), V_2O_5-TiO_2 (Rutile) and V_2O_5-ZrO_2 binary catalysts in 3-MP oxidation.

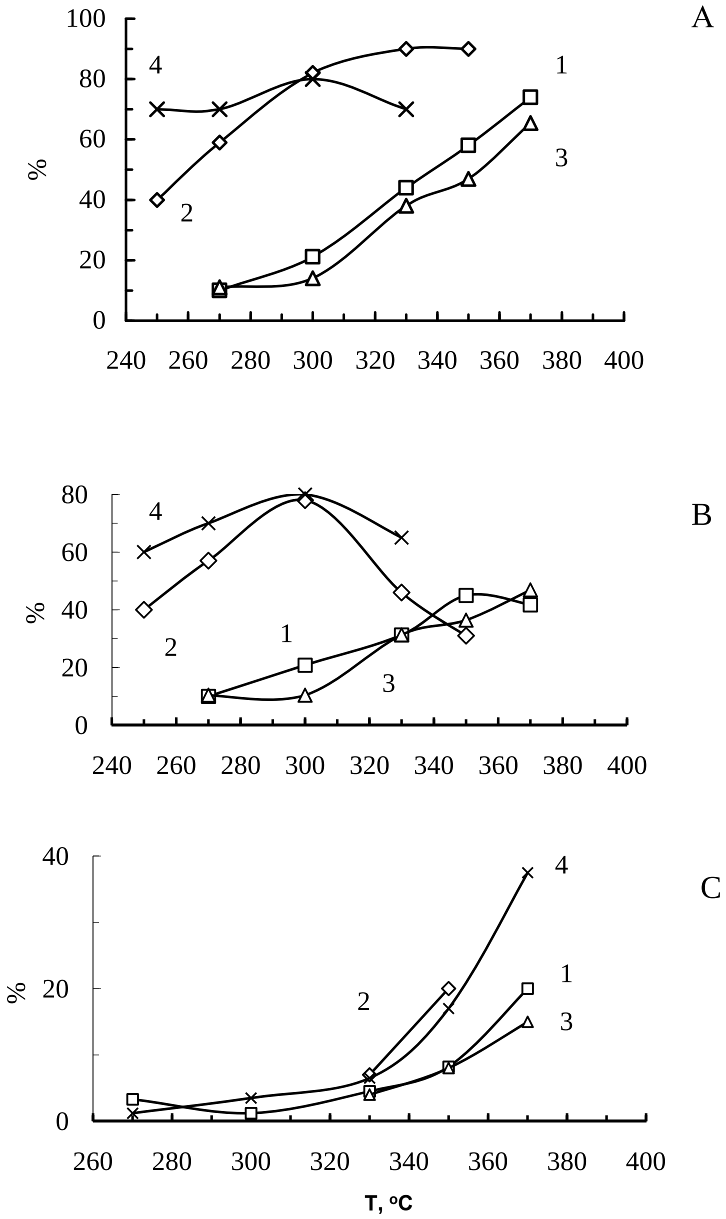
We investigated the general laws of the reaction, in particular, the effect of temperature, the amount of oxygen and water on the yield of the main products of the reaction.

The test of the vanadium-titanium oxide catalyst prepared using titanium dioxide with particle size of 200 nm showed that the feeding of initial substance (36,6 g), 550 L of air per 1 L of catalyst per hour in a temperature range of 250-350 °C, the conversion of 3-MP increases from 40 to 90%. The main product of the reaction was NA, the yield of which passes through a maximum with increasing temperature. While at 250 °C the yield of NA was 40-50%, then at 300 °C it reached 75%, a further increase in temperature causes a decrease in the yield of the targeted acid. It was noted that in the low-temperature region (250-300 °C) the selectivity for NA formation was 95%.



The feed rate of 3-MP – 36.6 g, air 420 L per 1 L of the catalyst in hour.
Mole ratio of initial substance:O_2:H_2O = 1:10:25.5 (1), 1:10:73 (2), 1:10:94 (3)

Figure 1 – Influence of temperature and amount of water on the conversion of 3-MP (A), yield (B) and selectivity of NA formation (C) under oxidation conditions over the $V_2O_5 \cdot 4TiO_2$ catalyst



The feed rate of 3-MP – 36,6 g, air 550 L, water 654,8 g. per 1 L of the catalyst in hour.
Mole ratio of 3-MP:O_2:H_2O = 1:13:94

Figure 2 – The effect of temperature and catalyst composition on the conversion of 3-MP (A), NA yield (B) and CO_2 (C) under oxidation conditions over the V_2O_5 (1), V_2O_5-TiO_2(Anatase) (2), V_2O_5-TiO_2(Rutile) (3), V_2O_5-ZrO_2 (4)

The variation in the water amount supplied to the reaction zone from 25 to 94 moles per mole of 3-MP practically does not affect the main parameters of the process: the conversion of the initial substance, the yield and the selectivity of the formation of the desired product. Figure 1 shows the results of the experiments with a lower air flow rate of 420 L per liter of catalyst in hour, corresponding to 10 moles of oxygen. It is shown that the conversion of 3-MP increased by 15% in the low-temperature region. At 250-270 °C, the yield of NA also increased. The selectivity of NA formation remained as high as 95%.

The tests of the binary vanadium-zirconium catalyst ($V_2O_5 \cdot 4ZrO_2$) were carried out in conditions comparable to the vanadium-titanium catalyst. The results obtained are shown in figure 2. Comparison of 3-MP conversion over two samples of the catalysts showed that when air was supplied at a rate of 550 L per liter of the catalyst in hour and at 250-270 °C, the activity of the vanadium-zirconium catalyst was higher than that in the vanadium-titanium catalyst. Somewhat higher was the yield of NA, the highest yield (70%) was obtained at 300 °C with feeding of water 76,0 and 97,0 moles per mole of 3-MP. The selectivity of NA formation at 270-300 °C was above 88%.

The injection of a smaller amount of air into the reaction zone (420 L per 1 L of catalyst in hour) resulted in a slight decrease in the conversion of the initial substance and the yield of NA. Despite this, the selectivity of NA formation even under these conditions remained high. In the oxidation products of 3-MP, in addition to NA, pyridine and nicotinic acid nitrile were present, but pyridine-3-aldehyde was not formed over both catalysts.

Figure 2 shows the comparison of 3-MP oxidation on the individual vanadium pentoxide and vanadium-titanium catalyst prepared on the basis of TiO_2 (Rutile). It is clearly seen that the V-Ti-O catalyst prepared using titanium dioxide with a higher dispersion particles (200 nm) and V-Zr-O catalyst significantly exceeds both vanadium pentoxide and vanadium-titanium contact containing TiO_2 (Rutile). These catalysts showed the high selectivity in the desired product formation and can be recommended for 3-MP oxidation into nicotinic acid.

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Резюме

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3-МЕТИЛПИРИДИННІҢ НИКОТИН ҚЫШҚЫЛЫНА БУКҮЙІНДЕ ТОТЫҒУЫНА ҚОЛДАНЫЛАТЫН БИНАРЛЫ V_2O_5–TiO_2 ЖӘНЕ V_2O_5–ZrO_2 КАТАЛИЗАТОРЛАРЫНЫҢ БЕЛСЕНДІЛІГІ

3-Метилпиридиннің парциалды қолданатын кейбір бинарлы V-Ti-O және V-Zr-O катализаторлардың каталитикалық белсенділігін зерттеу нәтижелері талқыланады.

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

Резюме

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КАТАЛИТИЧЕСКИЕ СВОЙСТВА БИНАРНЫХ СИСТЕМ V_2O_5–TiO_2 И V_2O_5–ZrO_2 В ПАРОФАЗНОМ ОКИСЛЕНИИ 3-МЕТИЛПИРИДИНА В НИКОТИНОВУЮ КИСЛОТУ

Обсуждены результаты исследования каталитической активности бинарных V-Ti-O и V-Zr-O катализаторов в парциальном окислении 3-метилпиридина.

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