

## Oxidation of 3- and 4-Methylpyridines on Vanadium-Anatase and Vanadium-Rutile Catalysts

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### Abstract

Heterogeneous catalytic vapor-phase oxidation of methylpyridines is “green”, the most simple and perspective method for obtaining pyridinecarboxylic acids. Vanadium-titanium catalysts have a wide application in some important industrial processes of oxidation.

Oxidation of 3- and 4-methylpyridine on vanadium-titanium catalysts has been investigated and for its preparation various titanium crystal modifications were used.

Characterization of the catalysts was carried out by using the X-ray diffraction,  $N_2$ -adsorption and thermal dissociation of  $V_2O_5$ . It was found that the use of anatase type of  $TiO_2$  with a higher BET surface area enhances the activity of the vanadium-titanium catalyst extremely. XRD-characterization of catalysts demonstrated that the only  $V_2O_5$  and anatase or  $V_2O_5$  and rutile phase was detected. It was established that the use of titanium dioxide of crystal modifications of anatase increases on the order of the dissociation rate  $V_2O_5$ .

It was shown that vanadium-titanium catalysts' activity and selectivity in investigated processes depends on  $TiO_2$  crystal modifications.  $V_2O_5$ -anatase is more active and selective in formation of pyridine carboxylic acids.  $V_2O_5$ -rutile in the process of oxidation of 4-methylpyridine on the catalyst forms the mixture of isonicotinic acid and its aldehyde. Connection between the dissociation rate of  $V_2O_5$  in catalysts of  $V_2O_5$ -anatase and  $V_2O_5$ -rutile and their activity in isomeric methylpyridines oxidation was established. High surface area, anatase structure of titanium are the key parameters determining the activity and selectivity of vanadium-titanium oxidation catalysts.

### Introduction

Heterogeneous catalytic oxidation of atmospheric oxygen is the main direction of oxidative petrochemical processing and coke and chemical hydrocarbon raw materials in oxygen-containing organic compounds [1].

Nicotinic acid (niacin) – Vitamin B3 and its derivatives are a group of biologically active compounds. Isonicotinic acid is the parent compound at receiving antituberculosis drugs (isoniazid). Nicotinic and isonicotinic acids and their derivatives are widely used in medicine, food industry, and in agriculture.

In order to create a one-step process of obtaining nicotinic and isonicotinic acid we have conducted the search for effective catalysts of vapor-phase oxidation of 3- and 4-methylpyridines.

Titanium dioxide is a component of a whole set of catalysts used in various oxidation processes [2-7]. It causes interest of researchers to the role of  $TiO_2$  catalytic effect of mixed catalysts. It is known [8], that  $TiO_2$  can exist in three polymorphic modifications (brookite, anatase and rutile) which differ from each other by structural type of a crystal lattice.  $TiO_2$  crystal modification can have a sufficient influence on its catalytic properties. Studying hydrogenation of CO on nickel-rutile and nickel-anatase catalysts showed that these catalysts differ by activity and structure of formed hydrocarbons [9]. In oxidation of toluene [10] anatase and rutile have exhibited various selectivity on partial oxidation products. When investigating oxidation of o-xylene in phthalic anhydride it is established, that substitution of anatase on rutile in vanadium-titanium oxide catalysts is accompanied by significant reduction in catalyst activity [11]. Previously [12] we have carried out a research of catalytic ac-

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tions of individual  $\text{TiO}_2$  modification in oxidation of 2-methyl-5-ethylpyridine. It was established, that the rate of dialkylpyridine transformation on anatase is 1.5-1.7 times higher, than on rutile.

In the process of creation of effective and stable working oxidation catalyst of organic compounds which includes titanium dioxide in its structure, possessing the ability to structural changes, it is necessary to take into account catalytic action of various  $\text{TiO}_2$  crystal modifications. This induced us to investigate catalytic action of vanadium-titanium catalysts, prepared from anatase and rutile, in oxidation of 3- and 4-methylpyridines.

## Experimental

3-Methylpyridine was used in the work, which had the following characteristics after distillation: boiling temperature  $141^\circ/690$  mm Hg,  $d_4^{20} = 0.9566$  and  $n_D^{20} = 1.5058$  and 4-methylpyridine with boiling temperature  $141^\circ/695$  mm Hg,  $d_4^{20} = 0.9547$  and  $n_D^{20} = 1.5058$ . Reduced characteristics corresponded to reference data.

Compound of vanadia-titania catalysts  $\text{V}_2\text{O}_5:\text{TiO}_2=1:16$  was prepared by mixture of vanadium and titan oxides in the corresponding molecular ratio. "Kronos" anatase and rutile from Aldrich were used for the preparation of catalysts. The obtained oxide mixture was carefully milled and pressed in the form of tablets 10 mm in diameter. Then the tablets were put into a muffle furnace "SNOL 8.2/1100" and calcined in air for 3 h at  $350^\circ\text{C}$ .

The X-ray diffraction (XRD) was carried out on a "DRON-7" diffractometer using Fe-K radiation with a scanning range ( $2\theta$ ) from  $20$  to  $40^\circ$ . In the prepared samples was determined anatase at  $31.9^\circ 2\theta$  and rutile at  $34.7^\circ 2\theta$ .

The catalytic tests were conducted in the flow-through fixed bed reactor with a reaction tube from stainless steel with 100-cm length and 20 mm in diameter. The reaction tube was in an electrically heated oven. 100 ml of the catalyst in the size of 3-5 mm was loaded into reactor. The air flow was controlled by a reometer. Before entering the oven, the air flows through a temperature-controlled device and exits saturated with 3- or 4-methylpyridines. Delivery rate of 3-methylpyridine is 37.8 g on 1l of the catalyst per hour. Water is pumped with a Vera Monostat pump through a steel tube into the oven, where it is mixed with the air and initial methylpyridines to give a reactant stream having a molar ratio of 1:7:85 at the beginning of the catalyst bed.

Unreacted methylpyridines and reaction products trapped water in scrubbers like airlift and analyzed by gas-liquid chromatography method. This renders it possible to determine the absolute concentration of the components in the liquid. Analysis of products of oxidation of 3- and 4-methylpyridines was carried out on chromatograph "LHM-8MD" with flame ionization detection. A metal column 2 m long and 3 mm in diameter was used. Lucopren G 1000, which was applied in the amount of 10% on Chromaton N-AW-HMDS (0.20-0.25 mm), was a stationary phase. The temperature of the column oven is  $140^\circ\text{C}$ , evaporator –  $230^\circ\text{C}$ , detector –  $230^\circ\text{C}$ .

Nicotinic and isonicotinic acids were detected by "pH-150MI" pH-meter and titration with 0.05 N KOH.

BET specific surface areas of the catalysts were measured by  $\text{N}_2$  adsorption using a Quantachrome Nova 1000e in liquid nitrogen at  $-195.8^\circ\text{C}$ .

Thermal dissociation of  $\text{V}_2\text{O}_5$  in vanadium-titanium catalysts was carried out on the installation shown in Fig. 1.

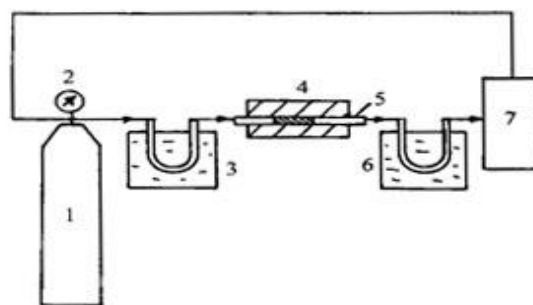


Fig. 1. Installation scheme for investigation of thermal dissociation of  $\text{V}_2\text{O}_5$ . 1 – cylinder, 2 – manometer, 3 – adsorber for clearing Helium, 4 – furnaces, 5 – quartz tube, 6 – absorber column with activated coal, 7 – chromatograph.

The weight of the sample (1 g) was carefully mixed in agate mortar, pressed on school press, crushed and placed in quartz tube which was blown by helium with constant speed and warmed up in the furnace at the temperature  $360-380^\circ\text{C}$  within 2 hours. Helium was preliminary cleared from  $\text{O}_2$  and  $\text{N}_2$  by their adsorption with activated coal at the temperature minus  $196^\circ\text{C}$ . Then the weight was moved to the second furnace with the temperature  $640-650^\circ\text{C}$  and immediately started storage of oxygen in absorber column filled with activated coal at the temperature –  $196^\circ\text{C}$  within 10 minutes. On storage termination an absorber column was quick-

ly warmed up by boiling water for desorption of stored oxygen which quantity was defined by chromatographic method on the installation with thermal conductivity detector. The column 1.5 m long and 3 mm in diameter is filled up with internal molecular sieves 5A (0.2-0.315 mm). The temperature of the column oven and detector is room, current of detector – 80 mA.

## Results and Discussion

At the present time for the oxidation of alkylaromatic compounds oxide vanadium-titanium catalysts of different composition are widely used. Earlier in the “A.B. Bekturov Institute of Chemical Sciences” JSC the catalyst [13] of the composition  $V_2O_5 \cdot 16TiO_2$ , which showed high activity and selectivity in the vapor-phase oxidation and oxidative ammonolysis of aromatic and heterocyclic compounds was developed. Therefore, in the reaction of vapor-phase oxidation of 3- and 4-methylpyridines under comparable conditions V-Ti-O-catalyst of  $V_2O_5 \cdot 16TiO_2$ , which were used for the preparation of anatase and rutile are tested.

Structure and phase composition of prepared catalysts was investigated by X-ray diffraction analysis. The X-ray diffractograms show (Fig. 2) that it consists of only the anatase and the  $V_2O_5$ -phase (catalyst A) or the rutile and the  $V_2O_5$ -phase (catalyst B). Thus, the anatase and rutile are not transformed and the interaction between the oxides during heat treatment was not observed.

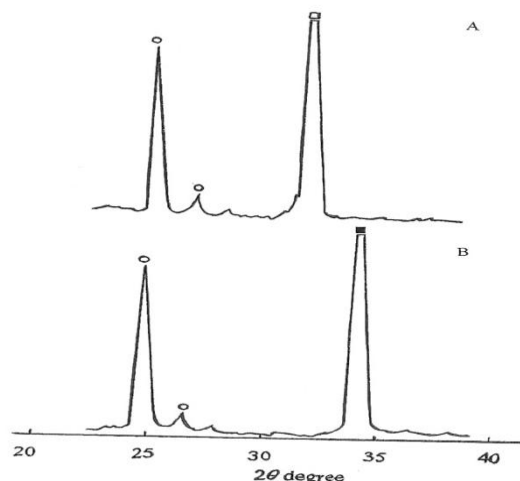


Fig. 2. XRD patterns of  $V_2O_5$ -anatase (A) and  $V_2O_5$ -rutile (B) catalysts.  $\circ$  –  $V_2O_5$ ,  $\square$  – anatase,  $\blacksquare$  – rutile.

Vanadium-titanium catalysts, for the preparation of which were used anatase and rutile, have been tested in comparable conditions in reaction of va-

pour-phase oxidation of 3- and 4-methylpyridines. Comparison of behavior of these samples of the catalyst has shown the influence of  $TiO_2$  crystal structure on their catalytic action in oxidation of 3-methylpyridine to nicotinic acid. Fig. 3 shows the dependence of conversion of 3-methylpyridine and yield of the main oxidation products from the temperature of reaction. The catalyst  $V_2O_5$ -anatase has higher activity in oxidative reaction processes. At temperature of 250°C the conversion of initial substance was 62.3%, and at temperature of 330°C – 100%, whereas on the catalyst with rutile even at the temperature of 330°C conversion does not reach 40%. On  $V_2O_5$ -rutile catalyst the maximal yield of an acid does not exceed 22% at the temperature of 330°C. On  $V_2O_5$ -anatase catalyst the greatest yield of nicotinic acid is 43-45% on initial 3-methylpyridine and 58.8-71.1% on reacted 3-methylpyridine at 230-250°C. You may notice that the oxidation processes using a catalyst containing anatase, occur more intensively than in the rutile catalyst. Not only higher conversion of initial 3-methylpyridine, but also greater formation of pyridine and carbon dioxide testifies about it (Fig. 3A, curve 5).

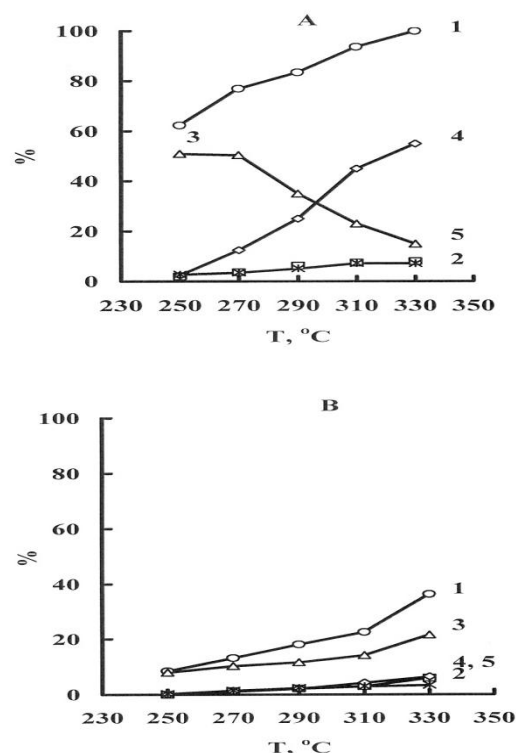


Fig. 3. Dependence of 3-methylpyridine conversion (1), the yield of nicotinic acid aldehyde (2), nicotinic acid (3), pyridine (4) and  $CO_2$  (5) from the temperature of 3-methylpyridine oxidation on  $V_2O_5$ -anatase (A) and  $V_2O_5$ -rutile (B).

Such character of  $\text{TiO}_2$  crystal structure influence on vanadium-titanium catalysts activity, prepared from anatase and rutile, is also observed in oxidation of 4-methylpyridine. As well as in case of 3-methylpyridine, the use of anatase in vanadium-titanium catalysts causes increase in catalytic activity of the system (Fig. 4), resulting in sharper growth of conversion of 4-methylpyridine. Also the processes of deep oxidation proceed more intensively on  $\text{V}_2\text{O}_5$ -anatase catalyst as it is evidenced by increase of the yield of  $\text{CO}_2$ . Thus, the output of carbon dioxide makes up 50% at  $290^\circ\text{C}$ , and while on the catalyst prepared from rutile, output of  $\text{CO}_2$  less than 7.5%. Catalyst on the basis of rutile is less active and has a milder effect, oxidizing 4-methylpyridine to isonicotinic acid and its aldehyde.

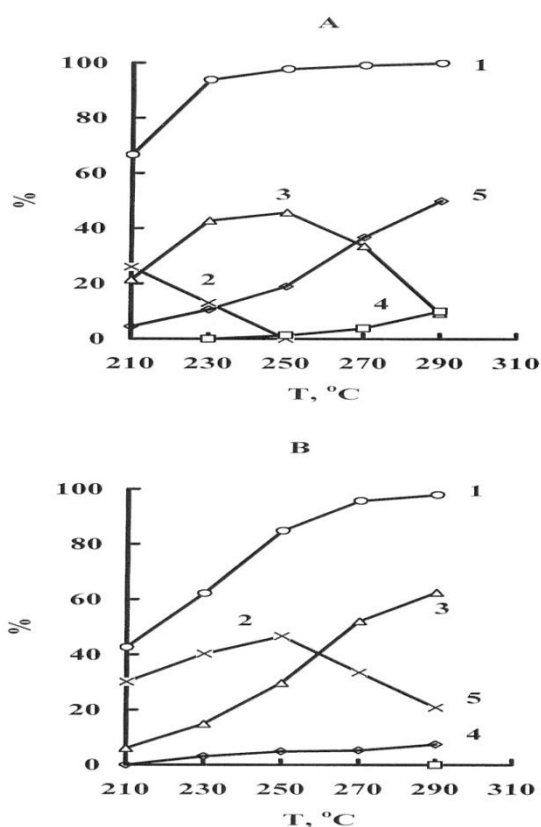


Fig. 4. Dependence of 4-methylpyridine conversion (1), the yield of isonicotinic acid aldehyde (2), isonicotinic acid (3), pyridine (4) and  $\text{CO}_2$  (5) from the temperature of 4-methylpyridine oxidation on  $\text{V}_2\text{O}_5$ -anatase (A) and  $\text{V}_2\text{O}_5$ -rutile (B).

The yield of isonicotinic acid aldehyde is 46.7% at  $250^\circ\text{C}$ , and on  $\text{V}_2\text{O}_5$ -anatase catalyst – no more than 26 % at the temperature of  $210^\circ\text{C}$ . The further rise in temperature results in transformation of formed aldehyde into isonicotinic acid, the yield of

which on this catalyst is 43-46%. The maximum yield of isonicotinic acid reaches 62.5% on vanadium-titanium catalyst, prepared from rutile, in more high-temperature area –  $290^\circ\text{C}$ .

Thus, a comparison of two samples of the catalytic action of V-Ti-O-contacts that contain  $\text{TiO}_2$  in modifications of anatase and rutile, showed that the catalytic activity of anatase (A) in the oxidation of the 3- and 4-methylpyridine is significantly higher than the catalyst with rutile (B). Increased activity of the catalyst A led to the fact that the temperature interval of its work shifted to a low-temperature region: for 3-methylpyridine from 330 to  $250^\circ\text{C}$ , and for 4-methylpyridine from 290 to  $230$ - $250^\circ\text{C}$ . For example, the highest yield of nicotinic acid (43-45%) was obtained at a temperature of  $250$ - $270^\circ\text{C}$ , and isonicotinic acid (50%) – at  $250^\circ\text{C}$ . On the catalyst A under these conditions in the reaction products a small aldehyde nicotinic acid (3%) is formed, and isonicotinic aldehyde was completely converted to isonicotinic acid. Catalyst B at this temperature, direct the reaction toward the mild oxidation and forming as aldehyde (46.7%), and also the isonicotinic acid (29.8%).

The activity of catalysts depends not only on the chemical composition, but also on the magnitude of their surface. In this regard, we have determined the specific surface of V-Ti-O-contacts containing  $\text{TiO}_2$  in anatase and rutile modifications. The data are presented in Table 1. It is evident that the catalyst A containing anatase has a specific surface  $17.78 \text{ m}^2/\text{g}$ , and the catalyst B on the basis of rutile –  $0.32 \text{ m}^2/\text{g}$ . This suggests that the high activity of the catalyst A in the oxidation of 3- and 4-methylpyridines is a consequence of larger specific surface of the contact.

**Table 1**  
BET – surface of vanadia-titania catalysts

Catalyst	Content (wt %)		BET – surface catalyst ( $\text{m}^2/\text{g}$ )
	$\text{V}_2\text{O}_5$	$\text{TiO}_2$	
$\text{V}_2\text{O}_5$ -anatase (A)	12.5	87.5	17.78
$\text{V}_2\text{O}_5$ -rutile (B)	12.5	87.5	0.32

The following examinations show to what extent other parameters influence the activity of vanadium-titanium catalysts.

It is known, that catalytic activity of vanadium oxide catalysts is defined by mobility of oxygen of

$V_2O_5$  lattice [14]. Vanadium pentoxide is capable to dissociate at the increased temperature. Oxygen release rate at its thermal dissociation characterizes a mobility degree of oxygen in lattice of vanadium (V) oxide and can be considered as a measure of its reactivity.

For an explanation of the received results catalytic activity of vanadium-titanium catalysts containing anatase and rutile, was compared to reactivity of vanadium (V) oxide in these catalysts which we judged by as a result of thermal dissociation of  $V_2O_5$ . So, for example, release rate of oxygen for  $V_2O_5$ -rutile catalyst is significantly less than for  $V_2O_5$ -anatase catalyst and accordingly equals to  $2.3 \cdot 10^{-3}$  and  $21.3 \cdot 10^{-3}$  mmole/gr·min (Fig. 5). As it is seen from the submitted results in Fig. 3 and 4,  $V_2O_5$ -anatase catalyst shows higher activity in reaction of oxidation of both 3-, and 4-methylpyridine.

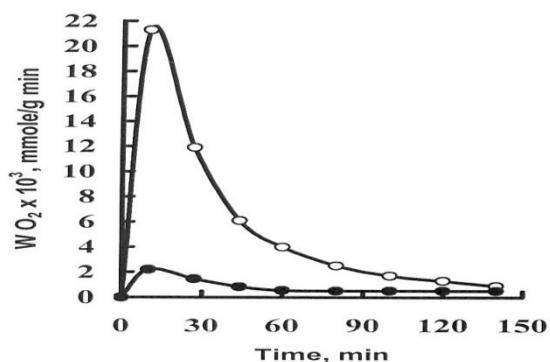


Fig. 5. Influence of  $TiO_2$  modification on dissociation rate of  $V_2O_5$  in  $V_2O_5$ -anatase (○) and  $V_2O_5$ -rutile(●) catalysts.

As it is known, titanium dioxide crystal modification differently influences on the connection character of superficial oxygen forms playing an essential role in activity and selectivity of vanadium-titanium oxide catalysts. So, for example, there are some data about weakening of V=O connection in case of using anatase and absence of such changes for rutile modifications [15]. Beside that the higher efficiency of vanadium catalysts, for the preparation of which anatase was used, in comparison with catalysts on the basis of rutile is connected with high concentration of vanadyl groups on the catalyst surface [16].

Comparison of oxygen release rate on binary vanadium-titanium catalysts, containing anatase and rutile, and their catalytic activity in oxidation of 3- and 4-methylpyridines testifies that there is a connection between catalytic activity of binary oxide systems and vanadium (V) oxide dissociation rate. Analysis of literature and experimental data

received in the process of studying the oxidation and oxidative ammonolysis of organic compounds on individual titanium dioxide crystal modifications and vanadium-titanium oxide catalysts having different structure, shows, that  $TiO_2$  crystal structure essentially influences on properties of the catalyst [5, 9-12]. It is more preferable to use anatase in oxidation of 3-methylpyridine because it is more active and selective regarding nicotinic acid. Catalysts, prepared from anatase, work at lower temperatures, than catalysts, which use rutile in their structure. In the process of oxidation of 4-methylpyridine on catalyst on the basis of anatase mainly isonicotinic acid is composed. The use of rutile catalyst promotes formation of a mixture of isonicotinic acid and its aldehyde.

## Conclusions

Investigation of catalytic properties of V-Ti-O-catalysts prepared from anatase and rutile, showed that  $V_2O_5$ -anatase with a higher BET surface area is more active in the oxidation of 3- and 4-methylpyridines.

It is established that the use of titanium dioxide of crystal modifications of anatase increases on the order of the dissociation rate  $V_2O_5$ . A correlation between the catalytic activity of vanadium-titanium catalysts and the rate of dissociation of vanadium oxide (V) is found.

The different  $TiO_2$  crystal modifications have a substantial influence upon the product yield of 3- and 4-methylpyridines oxidation.  $V_2O_5$ -anatase promotes the formation of nicotinic acid.  $V_2O_5$ -rutile directs the reaction toward the mild oxidation with formation of pyridine-4-aldehyde and isonicotinic acid.

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