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Optimization of vanadium-oxide catalyst for the oxidation of 3-methylpyridine into nicotinic acid

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Abstract: Upon modification of V_2O_5 with SnO_2 or ZrO_2, increase in the activity and selectivity of the vanadium-oxide catalyst in the vapor-phase oxidation of 3-methylpyridine into nicotinic acid were observed**.** It was shown that the promoting effects of SnO_2 and ZrO_2 were the result of increases under their influence of the proton affinity of the vanadyl oxygen and decreases in the enthalpy of deprotonation of the methyl group of the substrate, connected by a nitrogen atom with the Lewis acidic center (vanadium ion). The given characteristics were calculated by the Density Functional Theory quantum-chemical method. Modification of binary V_2O_5–SnO_2 and V_2O_5–ZrO_2–catalysts by TiO_2 addition resulted in a further increase in the nucleophility of the vanadyl oxygen and, as a consequence, an increase in the catalytic activity and selectivity for nicotinic acid formation.

Keywords: quantum-chemical method; oxidation; promoting effect; V_2O_5; SnO_2; ZrO_2.

INTRODUCTION

Nicotinic acid holds an important place among pyridine carboxylic acids,[1] based on which a number of medicinal preparations are obtained. Nicotinic acid is also used in the production of premixes in cattle breeding.

At present nicotinic acid is obtained industrially by a liquid-phase oxidation of 3-methylpyridine by inorganic oxidizers or by hydrolysis of nicotinic acid nitrile, formed upon ammoxidation of 3-methyl- or 2-methyl-5-ethylpyridines. Earlier, a catalyst for ammoxidation of 3-methylpyridine into nicotinonitrile,[2] which has been patented in 38 countries, was developed. This catalyst operates at the "Lonza" plant in Guangzhou (China). The disadvantages of this method are a two-stage process and the formation of harmful liquid wastes and gas emissions, containing ammonia.

A vapor-phase oxidation of methylpyridines by air oxygen on oxide catalysts is the most useful method for obtaining pyridine carboxylic acids. Increasing demands for nicotinic acid and its derivatives have promoted the interest of researchers to study the direct vapor-phase oxidation of 3-methylpyridine into nicotinic acid and to search for efficient catalysts for this process.[3–6]

Thus, on a V_2O_5–TiO_2–Na_2O catalyst with a V:Ti:Na atomic ratio of 100:20:1.15 at 400 °C, the maximum conversion of 3-methylpyridine into nicotinic acid was up to 94 % with a selectivity of 51 %.[7]

The vapor-phase oxidation of 3-methylpyridine was studied on vanadates of Y, Bi, Co, Fe, Mn,[8] and also Cr and Al.[8,9] It was shown that the largest total yield of nicotinic acid and pyridine-3-carbaldehyde attained 69 % at 350 °C on the $Cr_{0.5}Al_{0.5}VO_4$ vanadate.

This paper considers an experimental study of a number of catalysts, containing V_2O_5 and Sn, Zr and Ti dioxides in the vapor-phase oxidation of 3-methylpyridine. With the purpose of interpretation of the experimental results, a quantum-chemical study of the effect of oxide-modifiers upon the nucleophilic properties of the active oxygen connected with vanadium and the mobility of hydrogen of the methyl substituent of the initial substance chemisorbed on the catalyst surface was performed. The development of a one-stage heterogeneous catalytic process for the oxidation of 3-methylpyridine into nicotinic acid would enable the creation of new, more efficient, ecologically friendly and safe methods for the production of vitally important medicinal preparations.

EXPERIMENTAL

Materials

The initial 3-methylpyridine after drying and distillation had the characteristics, corresponding to the pure substance: boiling T / 140 °C (692 mm), $d_4^{20} = 0.9566$, $n_D^{20} = 1.5050$.

The catalysts with different contents of V_2O_5 and oxide-modifiers SnO_2, TiO_2 and ZrO_2 were prepared by mixing the initial oxides in the required molar ratio. Further, the obtained charge was pressed into tablets and calcined at 650–800 °C in an airflow for 2 h. The cooled catalysts were ground into grains with a size of 3–5 mm and 0.1 L was transferred to the reactor.

Synthesis experiments

The study of vapor-phase oxidation of 3-methylpyridine was performed in a flow-type unit with a metallic reactor of length 1000 mm and diameter 20 mm, simulating an element of an industrial contact machine. The feeding rate of 3-methylpyridine was 36 g per 1 L of catalyst per hour. The molar ratio of the reagents 3-methylpyridine:O_2:H_2O was 1:14:90. The reaction products were captured in air-lift type scrubbers.

Analysis of 3-methylpyridine oxidation products

The 3-methylpyridine was determined by a chromatographic method with a flame-ionization detector. The column was filled with sorbent 10 % Lucopren G 1000 on Chromatone N-AW-HMDS (0.20–0.25 mm). The column temperature was 140 °C, the

vaporator temperature was 230 °C) and helium was the gas carrier. A 0.1 % benzonitrile solution was used as the internal reference. Nicotinic acid was determined by KOH potentiometric titration using a universal ionomer pH-150MI.

The products of deep oxidation were analyzed by a chromatographic method with a thermal conductivity detector. Activated carbon «AG-5» (0.25−0.50 mm) was the adsorbent for the determination of CO, Polysorb-1 (0.16−0.20 mm) for the determination of CO_2. The temperature of the column-heating oven was 40 °C. In all experiments, the balance of the determined substances contributed 95−100 % of the total.

Computing details for quantum-chemical modeling

The active sites on the surface of the vanadium-oxide catalysts were simulated by clusters that contain tetrahedral coordinated ions of vanadium. The sizes of the V^{5+} vanadium cation, as is know from the literature,[10] allow both a tetrahedral and octahedral configurations. In this research on the influence of oxide-promoters, an initial V_4O_{10} cluster was used and one or two fragments of oxide-promoter molecules were sequentially added to this V_4O_{10} cluster. While studying the influence of the oxide-promoters on the deprotonation of $CH_3–$ groups, clusters with two atoms of vanadium were used to alleviate the calculations. It is considered that minimum surface clusters could be used for chemosorption research due to the strongly localized nature of the V=O and V–O bonds.[11,12] Optimization of clusters geometry was realized by the DFT method (Density Functional Theory)[13] using the two-exponential LanL2DZ basis set with an effective core potential.

For non-empirical calculations of energy and optimization of the geometry of the molecules, the Born–Oppenheimer approximation was used. This approximation does not consider the movement of the nucleus. For elimination of possible errors in the definition of energy and taking into account of the effects of molecular translation, rotation and vibration, frequency calculations for the clusters with optimized geometry were performed. By default, these calculations were realized at 298.15 K and 1 atmosphere pressure. To obtain a precise value of the total energy of a system at zero degrees Kelvin, the zero-point energy (*ZPE*) must be added to the received E_{tot}.[14] For comparison to the results of the experiment on the oxidation of 3-methylpyridine, the frequency calculations were performed at a reaction temperature of 573.15 K. The values of the thermal energy correction ($E_{therm.}$) received from the calculations was added to the total energy to take account of the effect of molecular translation, rotation and vibration motion at the specified temperature.

In accordance with the above, the proton affinity of vanadyl oxygen ($PA_{V=O}$) of the investigated clusters (Table I) was calculated by formula (1):

$$PA_{V=O} = [(E_{Neutral\ cluster} + E_{therm.Neutral\ cluster}) - (E_{Charged\ cluster} + E_{therm.Charged\ cluster})] \cdot 2625.5 \quad (1)$$

and enthalpy of deprotonation (*DE*) of the methyl group of adsorbed substrate (Table II) by formula (2):

$$DE = [(E_{anion/clus.} + E_{therm.anion/clus.}) - (E_{molecule/clus.} + E_{therm.molecule/clus.})] \cdot 2625.5 \quad (2)$$

The calculations were realized by the GAUSSIAN 09W program, version C.01.

RESULTS AND DISCUSSION

A comparison of the behaviors of the individual vanadium pentoxide, the binaries $V_2O_5–SnO_2, V_2O_5–ZrO_2$ and the three-component $V_2O_5–SnO_2–TiO_2$ and $V_2O_5–ZrO_2–TiO_2$ catalysts in oxidation of 3-methylpyridine is shown in Fig. 1. The experimental data testify to the fact that modification of V_2O_5 by the

above oxides resulted in a considerable increase in the catalyst activity, as could be judged by the significant increase in the conversion of 3-methylpyridine (A) and selectivity to nicotinic acid formation (B), as well as a decrease in the optimal reaction temperature.
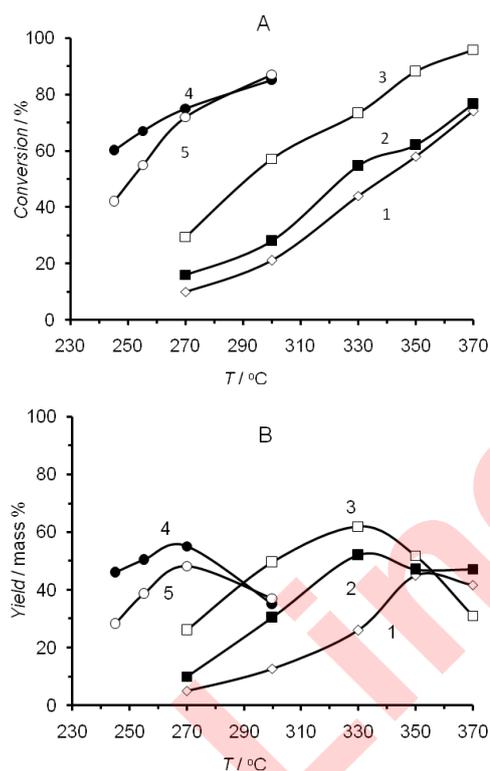
Fig.1. The effect of temperature and composition of the catalyst on the conversion of 3-methylpyridine (A) and yield of nicotinic acid (B) (1 - V_2O_5, 2 - V_2O_5–SnO_2, 3 - V_2O_5–ZrO_2, 4 - V_2O_5–SnO_2–TiO_2, 5 - V_2O_5–ZrO_2–TiO_2).

It is known[15] that SnO_2 may increase the mobility of the V=O bond in the V_2O_5 lattice, thus contributing to intensification of its dissociation and reduction to VO_2. It could be considered that in the vanadium–titanium catalysts with SnO_2 addition, this function of tin dioxide did not manifest itself because the extent of V_2O_5 reduction in the three-oxide vanadium–titanium–tin systems was approximately the same, or even less, than that in the two-component vanadium–titanium catalysts without SnO_2 additions. Probably, this is connected with the fact that SnO_2 may play the role of an oxidizer in relation to low vanadium oxides.[16] Due to this function of SnO_2 in the VO_2–SnO_2 system, an oxygen rearrangement is observed: tin dioxide is reduced to SnO, giving its oxygen for oxidation of VO_2 into V_2O_5, and the formed SnO is easily and rapidly oxidized by air oxygen again to SnO_2. Hence, it follows that SnO_2 may stabilize the structure of the oxide three-component system V_2O_5–SnO_2–TiO_2, giving its

oxygen to vanadium and facilitating re-oxidation of the catalyst by gas phase oxygen.

The results of the experiments for 3-methylpyridine oxidation on the vanadium–zirconium catalyst are also shown in Fig. 1, from which it could be seen that this catalyst was more efficient than V_2O_5. The promoting effect of ZrO_2 on the oxide-vanadium catalyst manifested itself in a significant increase in the conversion of the initial substance and in the yield of nicotinic acid. On the V_2O_5–ZrO_2 catalyst at 330 °C, the conversion of 3-methylpyridine and yield of nicotinic acid were 30–35 % higher than that on V_2O_5 without ZrO_2 addition. This showed that the binary V_2O_5–ZrO_2 catalyst was more active and selective than the V_2O_5–SnO_2 catalyst. The yield of nicotinic acid on the V_2O_5–ZrO_2 catalyst was 62 % (selectivity of 85 %).

An earlier study of the catalytic activity of V_2O_5–TiO_2 catalysts in the oxidation of 3-methylpyridines showed that V_2O_5 was markedly inferior in terms of catalytic activity and selectivity to nicotinic acid formation compared to those of oxide-vanadium catalysts modified by titanium dioxide. It was established that the addition of any quantity of TiO_2 to V_2O_5 sharply increased the efficiency of the catalyst activity. Thus, on the catalysts containing 18.1 and 77.7 % of TiO_2, the conversion of the initial pyridine base and selectivity to nicotinic acid formation increased 2–2.5-fold, and the yield of nicotinic acid increased almost five-fold as compared with the V_2O_5 catalyst.

The obtained results testify to the fact that an increase in activity and selectivity of the oxide-vanadium catalyst under the effect of TiO_2 additions is connected, in our opinion, with a change in the chemical and phase composition of the catalyst during its preparation and a change thereby of reactivity of the V_2O_5 oxygen. In the process of calcination of the catalysts in the system V_2O_5–TiO_2, a continuous series of solid solutions for VO_2–TiO_2 substitution are formed. Irrespective of the initial mixture composition, the VO_2–TiO_2 solid solution becomes a second main component of the catalyst alongside with V_2O_5. Tin dioxide seems to weaken the V=O bond in the lattice of vanadium pentoxide and contributes both to an acceleration of the transformation of V_2O_5 into VO_2, and the formation of new active centers on the catalyst surface, strengthening its oxidation ability and selectivity. Judging by the increase in activity and selectivity, the concentration of such centers on the surface of the vanadium oxide catalysts modified by TiO_2 is much higher than that on the surface of the vanadium oxide catalyst in the absence of TiO_2.

Non-stoichiometric vanadium oxides V_3O_7 and V_6O_{13}, formed on the surface of the vanadium–titanium catalysts in the process of oxidation reaction under the effect of the reaction medium may serve as active centers of V_2O_5–TiO_2 catalysts. Their formation was proved earlier by X-ray diffraction and IR spectroscopic measurements in a study of vanadium–titanium catalysts engaged

in the oxidation of 3-methylpyridine.[17] Hence, it follows that reactivity of vanadium pentoxide, modified by TiO_2 addition depends on the rate of mutual transfer in the system $V_2O_5 \Leftrightarrow V_3O_7 \Leftrightarrow V_6O_{13}$. The solid solution VO_2–TiO_2, which may be considered as the active carrier that changes the reactivity of V_2O_5, limits the rate in vanadium–titanium catalysts. The change of the mutual transfer rate in this system under the effect of the VO_2–TiO_2 solid solution determines the activity and selectivity of vanadium–titanium catalysts in dependence of the quantitative composition.

The above-stated was the basis for the selection of titanium dioxide as an additive to the binary V_2O_5–SnO_2 and V_2O_5–ZrO_2 catalysts.

The important value, characterizing the reactivity of oxygen bonded to vanadium, is its nucleophility. The calculated analog of nucleophility is the affinity of the vanadyl oxygen proton ($PA_{V=O}$). Using the DFT method, $PA_{V=O}$ values were obtained for clusters that model the active sites of V_2O_5 and of the modified V_2O_5–SnO_2, V_2O_5–ZrO_2, V_2O_5–SnO_2–TiO_2 and V_2O_5–ZrO_2–TiO_2.

Optimization of geometry of the clusters (Fig. 2) and calculation of the total energy values of the protonated $E_{tot.}(BH^+)$ and initial $E_{tot.}(B)$ structures were performed. The pentoxide vanadium model corresponds to the formula V_4O_{10} and is described by the D_{2h} symmetry group. The models containing $MO_2 = SnO_2$, TiO_2 and ZrO_2 promoters correspond to the formula MV_2O_7. The models with the given promoters possess C_{2V} symmetry. Upon protonation, the symmetry of all models decreases down to C_1. The models of the initial and protonated three-component catalysts possess C_1 symmetry.

According to quantum-chemical calculations, the simultaneous introduction in the V_4O_{10} cluster of two fragments of oxide-modifiers (SnO_2 and TiO_2 or ZrO_2 and TiO_2) (Fig. 2.) results in a considerable increase in the proton affinity of the vanadyl oxygen (Table I).

It was shown that indeed the proton affinity of the doubly-connected oxygen ($PA_{V=O}$ / kJ· mol^{-1}) increases in the same order as the catalytic activity, *i.e.*, $V_2O_5 < V_2O_5$–$SnO_2 < V_2O_5$–$ZrO_2 < V_2O_5$–SnO_2–$TiO_2 < V_2O_5$–ZrO_2–TiO_2. Results of the calculations are given in Table I.

Based on the regularities of the effect of the oxide-modifiers, revealed by experimental result and quantum-chemical calculations, a catalyst for direct vapor-phase oxidation of 3-methylpyridine into nicotinic acid and a waste-free technology of its preparation were developed.[18]

The present approach to the interpretation of the experimental results by the relative activity of the studied catalysts in the oxidation of 3-methylpyridine was based on the concepts of organic CH-acids and the theories of adsorption and catalysis on the surface of transient metal oxides.
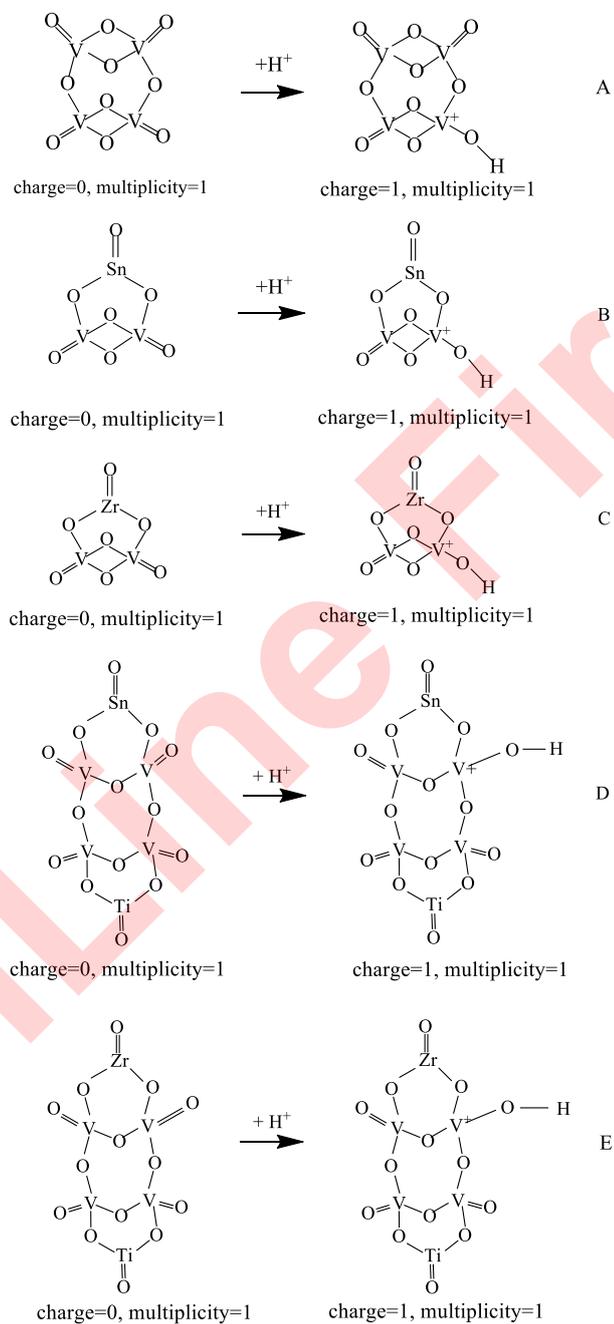
Fig. 2. Clusters modeling active centers of V_2O_5 (A), V_2O_5–SnO_2 (B), V_2O_5–ZrO_2 (C), V_2O_5–SnO_2–TiO_2 (D) and V_2O_5–ZrO_2–TiO_2 (E).

TABLE I. Total energy ($E_{tot.}$) and thermal energy ($E_{therm.}$) of vanadium-containing clusters and their charged forms (Fig. 3), proton affinity of oxygen, bonded to vanadium-ion ($PA_{V=O}$). Temperature 573.15 K

Clusters	$-E_{tot.}$ / a.u.	$E_{therm.}$ / a.u.	$PA_{V=O}$ / kJ·mol^{-1}
A:			
Neutral cluster	1038.17019	0.08145	
Charged cluster	1038.45849	0.09380	724.5
B:			
Neutral cluster	672.90766	0.05559	
Charged cluster	673.20234	0.06791	741.3
C:			
Neutral cluster	716.26601	0.05583	
Charged cluster	716.58135	0.06826	795.3
D:			
Neutral cluster	1400.87024	0.11778	
Charged cluster	1401.18833	0.13014	802.7
E:			
Neutral cluster	1444.17841	0.11795	
Charged cluster	1444.56402	0.13034	979.9

As it is known,[19] 3-methylpyridine is a weak CH-acid (AH) and under the effect of a proton acceptor (B) may release the proton with the formation of the corresponding carbanion (A$^-$). The heat of the reaction of proton transfer from CH-acid to the nucleophilic center of the catalyst surface is determined from the equation:
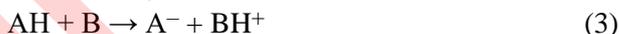
$$AH + B \rightarrow A^- + BH^+ \tag{3}$$
$$\Delta E = E_{tot.}(A^-) + E_{tot.}(BH^+) - E_{tot.}(B)$$

where $E_{tot.}$ is the total energy of the corresponding compound.

For the same CH-acid (3-methylpyridine), the heat of the proton transfer reaction depends on proton affinity of the base (B), which is determined from the equation:

$$B + H^+ \rightarrow BH^+ \tag{4}$$
$$PA = E_{tot.}(BH^+) - E_{tot.}(B) - E(H^+)$$

where: *PA* is the proton affinity and $E(H^+)$ is the energy of proton formation.

Therefore, the $E_{tot.}(BH^+) - E_{tot.}(B)$ difference, or proton binding energy, differs from proton affinity to base B by a constant value $E(H^+)$, and may serve as a characteristic of the proton acceptor activity (in the present case, the vanadyl oxygen).

Modeling of the «vertical» adsorption of 3-methylpyridine by a nitrogen atom at a Lewis acidic center (vanadium ion) with methyl proton transfer to the vanadyl oxygen was performed (Fig. 3). It was established that the enthalpy of

deprotonation of the chemisorbed substrate (DE / kJ·mol^{-1}) decreased in the order $V_2O_5 > V_2O_5$–$SnO_2 > V_2O_5$–TiO_2 (Table II). According to the experimental data, an activity of the catalysts in the oxidation of 3-methylpyridine increased in the same order.
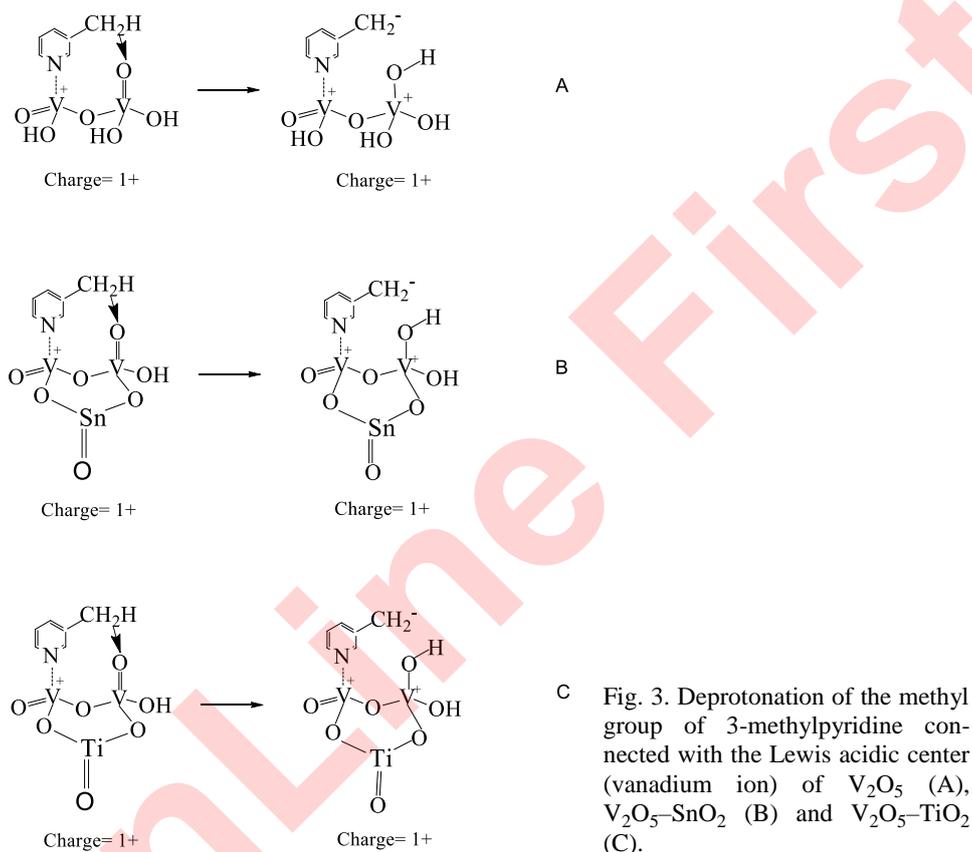
Fig. 3. Deprotonation of the methyl group of 3-methylpyridine connected with the Lewis acidic center (vanadium ion) of V_2O_5 (A), V_2O_5–SnO_2 (B) and V_2O_5–TiO_2 (C).

TABLE II. Total energies ($E_{tot.}$) and thermal energy ($E_{therm.}$) of 3-methylpyrine and its carbanion, connected with the vanadium pentoxide and binary catalysts and deprotonation enthalpy (DE) of the substrate. Temperature 573.15 K

Structure	$-E_{tot.}$ / a.u.	$E_{therm.}$ / a.u.	DE / kJ·mol^{-1}
A:			
Molecule/cluster	883.49487	0.22557	
Anion/cluster	883.40403	0.22342	232.9
B:			
Molecule/cluster	960.89283	0.21200	
Anion/cluster	960.80488	0.20965	224.7
C:			
Molecule/cluster	1015.75760	0.21260	

Anion/cluster	1015.67325	0.21036	215.6

CONCLUSIONS

The results of the quantum-chemical calculations complied with the experimental data on the promoting effect of additions of SnO_2, TiO_2 and ZrO_2 to V_2O_5 in the oxidation of 3-methylpyridine. According to the calculations, the mechanism of the promoting effect of the studied oxide-modifiers is determined by their ability to increase the nucleophility of the vanadyl oxygen and to decrease the deprotonation enthalpy of the methyl group of the chemisorbed 3-methylpyridine.

Catalyst for direct vapor-phase oxidation of 3-methylpyridine into nicotinic acid and a waste-free technology of its preparation was developed. The catalytic oxidation of 3-methylpyridine on the developed catalyst was tested on a pilot unit. The yield of nicotinic acid attained was 75–77 % (selectivity 90 %).

И З В О Д
ОПТИМИЗАЦИЈА ОКСИДАЦИЈЕ 3-МЕТИЛПИРИДИНА У НИКОТИНСКУ КИСЕЛИНУ КАТАЛИЗОВАНУ ВАНАДИЈУМ-ОКСИДОМ

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После модификација V_2O_5 помоћу SnO_2 и ZrO_2 уочено је повећање селективности у оксидацији 3-метилпиридина у никотинску киселину, у гасовитој фази, помоћу ванадијум-оксида. Показано је да услед присуства SnO_2 и ZrO_2 долази до повећања афинитета према протону атома кисеоника у ванадијум-оксиду, и да је смањивање енталпије депротоновања метил-групе супстрата повезано са везивањем атома азота супстрата за Луисову киселину (ванадијум јон). Ове карактеристике израчунате су квантно-хемијским поступцима теорије функционала густине (Density Functional Theory). Модификацијама бинарних катализатора V_2O_5–SnO_2 и V_2O_5–ZrO_2 додавањем TiO_2 повећава се нуклеофилност ванадил кисониковог атомашто има за последицу повећавање каталитичке активности и селективности у синтези никотинск екиселине.

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