

Catalytic Oxidation of 4-Methylpyridine on Modified Vanadium Oxide Catalysts

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ABSTRACT: Reaction of gas-phase oxidation of 4-methylpyridine on individual V_2O_5 , binary and ternary vanadium-oxide catalysts was studied. These catalysts were modified by additives of SnO_2 and TiO_2 . It was found that modifying V_2O_5 leads to increase in the activity of binary contacts. Upon transition from binary $V_2O_5-SnO_2$ and $V_2O_5-TiO_2$ catalysts to the ternary system of $V_2O_5-TiO_2-SnO_2$, a higher increase in activity is observed. This extension in activity leads to increase conversion of initial substance and shifting the maximum yield of intermediate pyridine-4-carbaldehyde and isonicotinic acid to the low-temperature area. To research the mechanism of promotion, we used the quantum chemical method of Density Functional Theory. It was found that the promoting effect of SnO_2 and TiO_2 was caused by increasing a proton affinity of vanadyl oxygen ($PA_{V=O}$). Upon transition from binary clusters to the ternary system of $V_2O_5-TiO_2-SnO_2$ the synergism effect is observed. It is shown that by transfer of a proton to vanadyl oxygen and formation of a new O-H bond the energy is emitted. This energy compensates a heterolytic C-H bond cleavage. It was found that the promoting effect of SnO_2 and TiO_2 causes the decrease of deprotonation enthalpy of the methyl substituent of the chemisorbed substrate. The results of the calculations agree with the experimental data on the influence of oxide modifiers on activity and selectivity of the studied catalysts in 4-methylpyridine oxidation.

KEYWORDS: 4-Methylpyridine; Oxidation; Vanadium oxide catalyst; Mechanism; Density Functional theory.

INTRODUCTION

Isonicotinic acid and its derivatives possess a big variety of valuable physiologically active properties. They have broad application as antitubercular drugs and also stimulators of growth and maturing of many crops. Isonicotinic acid is received by liquid-phase oxidation of 4-methylpyridine and its methylol derivatives of nitric acid [1]. Gas-phase catalytic oxidation of 4-methylpyridine by oxygen air on the oxide catalysts are the most effective method of obtaining pyridine-4-carbaldehyde and isonicotinic acid.

This gas-phase catalytic oxidation process allows receiving valuable target products from initial raw materials in one stage. For that reason, this process causes an interest in a large number of researchers. Moreover, the vanadium-oxide catalysts modified by various oxides are widely used [1-5].

So, on the catalyst with a ratio $V_2O_5:Cr_2O_3$:pumice=33.06:10.64:100 isonicotinic acid is received with the yield of 38.6 % and selectivity of 65.0 % at

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a temperature of 360 °C. In similar conditions on the catalyst with a ratio $V_2O_5:Fe_2O_3:pumice=33.06:10.64:100$ the yield and selectivity of formation of isonicotinic acid was 37.4 and 77.0 %, respectively [6]. By oxidation of 4-methylpyridine on the $V_2O_5/kieselguhr$ catalyst at a temperature of 350 °C, isonicotinic acid and CO_2 are obtained with a yield of 71.6 % and 4.7 %, respectively [7].

On the $(VO)_2P_2O_7$ catalyst at a temperature of 410–430°C and a molar ratio 4-methylpyridine: $O_2:H_2O=1:10:100$, the conversion of initial substance was 84 %, the pyridine-4-carbaldehyde yield was 70 % (selectivity 83.3 %) [8]. Oxidation of 4-methylpyridine on V-Si-Al-P-oxide catalysts of various compositions allows receiving pyridine-4-carbaldehyde with the yield of 60–95 % [9].

In paper [10] isonicotinic acid with the yield of 82 % was synthesized by vapor-phase oxidation of 4-methylpyridine over V-Ti-Cr-Al-P catalyst at the molar ratio 4-methylpyridine: $O_2:H_2O=1:96:70$ and temperature of 310 °C. Influence of reaction temperature, loads, amount of water and oxide promoters on catalytic characteristics was studied. It was found that acidic promoter can increase catalyst's productivity, but alkaline oxide, contrary, reduce its activity.

In patent [11] isonicotinic acid with the yield of 18-38 % was received by oxidation of 4-methylpyridine on the vanadium-titanium catalyst containing oxides of vanadium and titanium at the following masses components ratio %: $V_2O_5:TiO_2(anatase)=(5-50):(95-50)$.

The quoted publications for 4-methylpyridine gas-phase oxidation on the modified oxide vanadium catalysts give the representation of the reached results for this process.

This article is devoted to research a number of the catalysts containing V_2O_5 , SnO_2 , and TiO_2 in the gas-phase oxidation of 4-methylpyridine. The experimental results were interpreted by quantum chemical computation. The influence of oxide modifiers on nucleophilic properties of vanadyl oxygen was studied. Also, the influence of oxide modifier on the deprotonation enthalpy of methyl group chemisorbed substrate was investigated.

EXPERIMENTAL SECTION

Initial pure 4-methylpyridine after drying and distillation had the characteristics (B.p. 141 °C/695 mm, $D_4^{20}=0.9547$, $n_D^{20}=1.5058$).

The catalysts with different content of V_2O_5 and oxides-modifiers SnO_2 and TiO_2 were prepared by mixing the initial oxides in the required molar ratio. 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 flow for 2 h at 600 °C.

The catalytic tests were conducted in the flow-through fixed bed reactor with a reaction tube from stainless steel with 120-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 the reactor. The air flow was controlled by a rheometer. Before entering the oven, the air flows through a temperature-controlled device and exits saturated with 4-methylpyridine. The delivery rate of 4-methylpyridine is 37.5 g on 1 liter of the catalyst per hour. Water is pumped with a Reglo Analog MS-2/8-160 through a steel tube into the oven, where it is mixed with the air and initial 4-methylpyridine to give a reactant stream having a molar ratio of 1:14:110 at the beginning of the catalyst bed.

Products of reaction were caught in the airlift type scrubbers irrigated by water. Chromatographic analysis of oxidation products of 4-methylpyridine was carried out by chromatograph «Cvet-106» with flame ionization detector. The gas-carrier was argon. The glass column 1000 mm long and with a diameter of 4 mm is filled with a stationary liquid phase of 25 % of polyethylene adipate + 2 % of H_3PO_4 on the INZ-600 diatomite carrier. The column thermostat temperature 125 °C, the temperature of evaporator 200 °C. As the internal standard, we used 2,4,6-kollidin.

Isonicotinic acid was detected by "pH-150MI" pH-meter and titration with 0.05 N KOH.

Products of deep oxidation were analyzed on the LHM-8MD chromatograph with the heat conductivity detector. The stainless steel columns have a length of 3.5 m and an internal diameter of 3 mm. As adsorbent for detection of CO was AG-5 absorbent coal (0.25–0.50 mm), for CO_2 – polisorb-1 (0.16–0.20 mm). The columns temperature of the thermostat was 40 °C. In all experiments, the balance on the defined substances was 95–100 %.

Optimization of clusters geometry was carried out by the method of density functionality (DFT, Density Functional Theory) [12]. By this method in quantum and

chemical calculations of the structure and electronic properties of the transitional metals oxides most widely used the B3LYP approach [13–15]. This approach is based on hybrid functionality in which exchange energy calculates by the attraction of the exact result received by the Hartree-Fock method. We used the two-exponential LanL2DZ basic set with an effective core potential. The calculations were carried out by the Gaussian 09W license program, version D.01.

RESULTS AND DISCUSSION

The results of testing the individual V_2O_5 , binary $V_2O_5-SnO_2$, and $V_2O_5-TiO_2$, and also ternary $V_2O_5-TiO_2-SnO_2$ catalysts in the oxidation of 4-methylpyridine are given in Figs. 1, 2.

According to experimental data (Fig. 1) conversion of 4-methylpyridine increases in the following row of catalysts: $V_2O_5 < V_2O_5-SnO_2 < V_2O_5-TiO_2$. In the same row, the reactivity of methyl substituent is increasing, indicated by the position of maximum yield of pyridine-4-carbaldehyde and isonicotinic acid at the variation of the reaction temperature. Thereby, it shows that modification of V_2O_5 with dioxides of tin and titanium brings to increase the catalytic activity.

It is known [16], that SnO_2 may increase the mobility of the V=O bond in the V_2O_5 lattice, thus contributing to the intensification of its dissociation and reduction to VO_2 . One may consider that in the vanadium-titanium catalysts with SnO_2 addition this function of tin dioxide has not manifested itself, because of an extent of V_2O_5 reduction in the oxide three-component, $V_2O_5-TiO_2-SnO_2$ system has been approximately the same, and even less, than that in the two-component $V_2O_5-TiO_2$ catalysts without SnO_2 additions. Probably it is connected with the fact that SnO_2 may play the role of an oxidizer in relation to low vanadium oxides [17]. Due to this function of SnO_2 in the VO_2-SnO_2 system, an oxygen rearrangement is observed: SnO_2 is reduced to SnO , giving off its oxygen for oxidation of VO_2 into V_2O_5 , and the formed SnO is easily and rapidly oxidized by the 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 off its oxygen to vanadium and facilitating re-oxidation of the catalyst by the gas phase oxygen.

The obtained results demonstrate that TiO_2 , not being the good oxidizing agent, while modifying, gives to V_2O_5

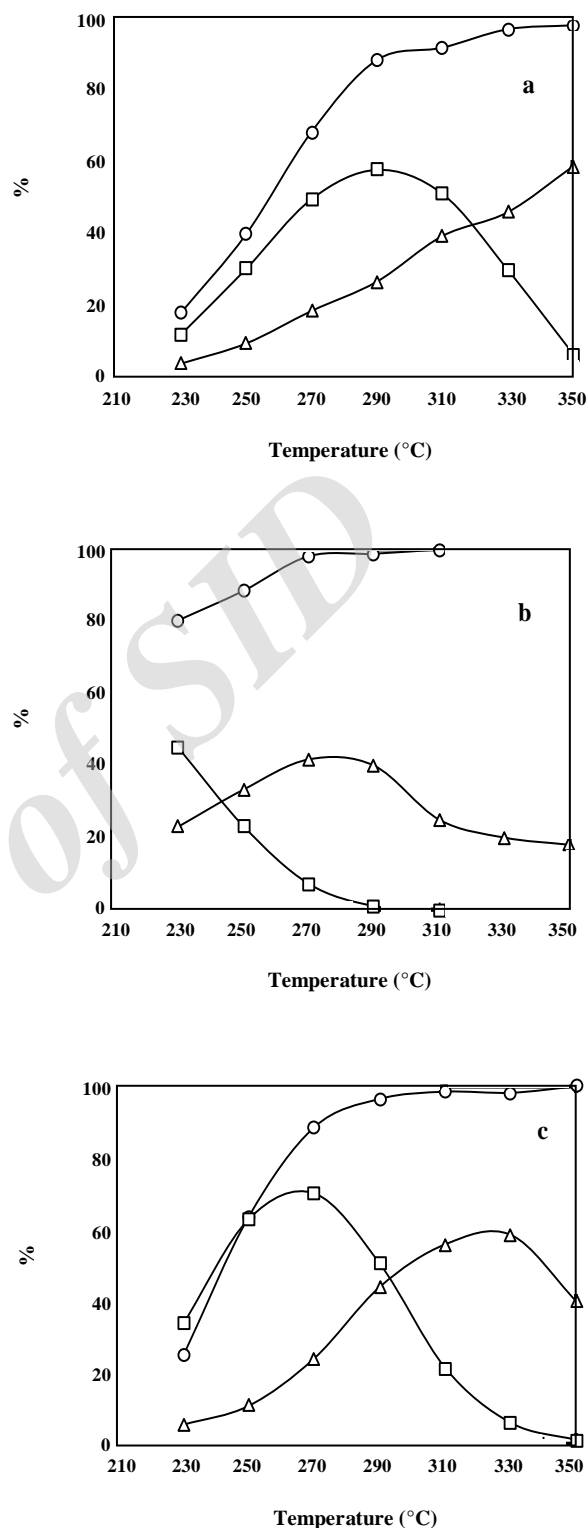


Fig. 1: The effect of temperature on the conversion of 4-methylpyridine (\circ), the yield of pyridine-4-carbaldehyde (\square) and yield of isonicotinic acid (Δ) in 4-methylpyridine oxidation on V_2O_5 (a), $V_2O_5-TiO_2$ (b), $V_2O_5-SnO_2$ (c) catalysts.

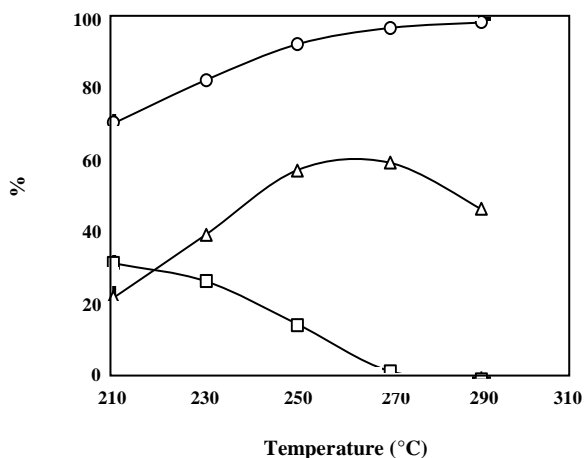


Fig. 2: The effect of temperature on the conversion of 4-methylpyridine (○), the yield of pyridine-4-carbaldehyde (□) and yield of isonicotinic acid (Δ) in 4-methylpyridine oxidation on V_2O_5 - TiO_2 - SnO_2 catalyst.

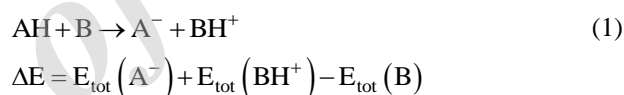
new catalytic properties in the oxidizing process. Increasing the activity of the vanadium oxide catalyst under the influence of TiO_2 additives, in our opinion, is connected with the change of chemical and phase composition of the catalyst during its preparation. This change influences the reactionary ability of V_2O_5 oxygen. In the process of calcination of the catalysts in the V_2O_5 - TiO_2 system a continuous number of substitutional solid solutions of V_2O_5 - TiO_2 is formed. Regardless of the composition of the initial mixture, a substitutional solid solution of TiO_2 - VO_2 becomes the second major component of the catalyst along with V_2O_5 . Titan dioxide, apparently, weakens the $V=O$ bond in the lattice of V_2O_5 and promotes both accelerations of transformation V_2O_5 to VO_2 , and formation at the surface of the catalyst the new active centers, increasing its oxidizing and selective ability. Judging by an increase of 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 V_2O_5 surface.

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 the V_2O_5 - TiO_2 catalysts. Their formation was proved by us earlier by the methods of X-ray diffraction and IR-spectroscopy upon the study of the vanadium-titanium catalysts, engaged in oxidation [18]. Hence, it follows that reactivity of vanadium

pentoxide, modified by TiO_2 additions 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 an active carrier, changing reactivity of V_2O_5 , limits the rate in the 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 the vanadium-titanium catalysts independence of the quantitative composition.

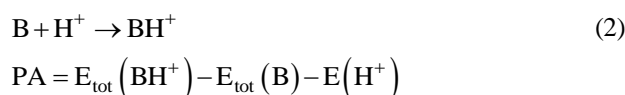
When modeling the chemisorption of 4-methylpyridine on the Lewis acidic centers of binary catalysts we proceeded from the following: initial substance has basic properties [19] and is capable to interact with the Lewis acidic centers of the catalyst surface.

As it is known [20], 4-methylpyridine is a weak CH-acid (AH) and under the effect of a proton acceptor (B) may give it off with the formation of a 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:



Where E_{tot} - the total energy of the corresponding compound.

For one and the same CH-acid (4-methylpyridine) the heat of the proton transfer reaction shall depend on the proton affinity of the base (B), which is determined from the equation:



where: PA - proton affinity, $E(H^+)$ - the energy of proton formation.

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

It is generally accepted that activity and selectivity of the vanadium-oxide catalysts for oxidation of hydrocarbons is connected with the presence of various forms of oxygen on a surface of the catalyst, and the large role is played by double bonded vanadyl oxygen of a lattice ($V=O$). One of the reasons for promoting the effect of dioxides of tin and titanium to the catalytic activity

modified vanadium-oxide contacts can be the increase under their influence the nucleophilicity (affinity to a proton) of the vanadyl oxygen, which participates in a proton detachment from the oxidized methyl substituent.

For a theoretical assessment of various oxide promoters influence on proton affinity of the oxygen, bonded with vanadium, quantum chemical calculations were carried out. Quantum chemical study of catalytic reactions at present time is conducted by the use of the elementary cluster models, at the same time the active center is modeled by one or two atoms of the catalyst. Application of similar models is very attractive when studying the mechanism of catalytic reactions. However, these models cannot be used for predicting the catalytic properties because the catalyst is not represented to them as a solid body. Excessive simplification of the model depreciates the quantum and chemical prediction. Complications of the model and attempts to adequately transfer solid-state characteristics of the catalyst are connected with the sudden increase in computing difficulties. The active centers of the studied catalysts, which play a role of acceptors of a proton, modeled by clusters, contain fragments of V_2O_5 and oxide promoters. The minimum surface clusters could be used for chemisorption research due to the strongly localized nature of V=O и V-O bonds [21, 22].

Proton affinity was estimated by a difference of total energies of the initial and protonated clusters with the optimized geometry, i.e. energy which is emitted as a result of the accession of a proton to vanadyl oxygen.

Calculations showed that proton affinity (nucleophilicity) of vanadyl oxygen for the clusters, modeling the active centers of vanadium pentoxide and catalysts promoted by TiO_2 and SnO_2 (Table 1) increases in the row: $V_4O_{10}(756.6) < V_2O_5-SnO_2(773.7) < V_2O_5-TiO_2(779.4)$.

Upon transition from binary $V_2O_5-SnO_2$ and $V_2O_5-TiO_2$ clusters to ternary $V_2O_5-TiO_2-SnO_2$ system the synergism effect is observed. The summarizing impact of two oxide promoters on proton affinity of vanadyl oxygen ($PA_{V=O}$) significantly surpasses effects of each separate promoter in binary clusters (Table 1, q - charge, m - multiplicity).

For studying the influence of oxides modifiers on the reactionary ability of methyl group we modeled chemisorption of 4-methylpyridine on the Lewis acidic centers of V_2O_5 and binary catalysts. Calculations

showed (Table 2) that energy E_{C-H} of a heterolytic cleavage of C-H bond of the methyl group of a substrate adsorbed on the Lewis acidic centers of V_2O_5 is $1063.7 \text{ kJ}\cdot\text{mol}^{-1}$. At proton transfer on vanadyl oxygen with formation of new O-H bond energy is emitted. This energy compensates a heterolytic C-H bond cleavage.

As a result, the enthalpy of deprotonation of the methyl group is $155.7 \text{ kJ}\cdot\text{mol}^{-1}$. Modification of vanadium pentoxide by additives of SnO_2 and TiO_2 leads to decrease in enthalpy of deprotonation of the methyl substituent of a chemisorbed substrate (Table 2). Results of calculations agree with the experimental data on the influence of oxide modifiers on activity and selectivity of the studied catalysts in 4-methylpyridine oxidation.

At vertical adsorption and activation of 4-methylpyridine the substituent is becoming far from the surface oxygen, and for its oxidation, transfer of the reactionary center to methyl group is necessary. At adsorption of a substrate by the ring plane on the Lewis acidic center, the methyl substituent is situated at the distance from a surface allowing chemical interaction with active oxygen of a surface (Table 2). Our calculations for this option of ternary adsorption gave a close DPE value ($163.5 \text{ kJ}\cdot\text{mol}^{-1}$).

Modifying V_2O_5 with simultaneous addition of SnO_2 and TiO_2 leads to an increase in the activity of the ternary catalytic system in the oxidation reaction of 4-methylpyridine, in comparison with binary contacts (Fig. 2). It is possible to estimate it by the shifting of maximum yield of pyridine-4-carbaldehyde and isonicotinic acid to the low-temperature area, and also by decreasing in temperature at which intermediate aldehyde disappears as a product of the reaction.

CONCLUSIONS

Individual V_2O_5 , binary $V_2O_5-SnO_2$ and $V_2O_5-TiO_2$, and also ternary $V_2O_5-TiO_2-SnO_2$ catalysts are tested in vapor-phase oxidation of 4-methylpyridine.

Modifying V_2O_5 with dioxides of titanium and tin leads to increase in the catalytic activity of the obtained systems, at the same time, the synergy effect is observed upon transition from binary catalysts to the ternary system.

It was found that the promoting effect of SnO_2 and TiO_2 is caused by increasing the proton affinity of the vanadyl oxygen ($PA_{V=O}$) under their influence and also decrease the enthalpy of deprotonation of the chemisorbed substrate methyl substituent.

Table 1: Total energies of V-contained clusters and their protonated forms ($E_{tot.}$), proton affinity of the oxygen bounded to vanadium ion (PA), designed by DFT method (B3LYP/LanL2DZ).

No	Reaction	$-E_{tot.}$, a.u.		PA*,
		Initial cluster	Protonated cluster	$\text{kJ}\cdot\text{mol}^{-1}$
a	<p style="text-align: center;">$q=0, m=1$ $q=1, m=1$</p>	1038.1702	1038.4584	756.6
b	<p style="text-align: center;">$q=0, m=1$ $q=1, m=1$</p>	672.9077	673.2023 (1)	773.7 (1)
c	<p style="text-align: center;">$q=0, m=1$ $q=1, m=1$</p>	727.7569	728.0537 (2)	779.4 (2)
d	<p style="text-align: center;">$q=0, m=1$ $q=1, m=1$</p>	1400.8702	1401.1883 (1) 1401.1699 (2)	835.1 (1) 786.8 (2)

* $1 - PA = (E_{init} - E_{prot}) \times 2625,5$

Table 2: Total energies connected with V_2O_5 and binary catalysts of 4-methylpyridine and its carbanion (E_{tot}), the energy of a heterolytic C-H (E_{C-H}) bond cleavage, enthalpy of deprotonation of the substrate (DPE) with the transfer of a proton to vanadyl oxygen, calculated by the DFT method (B3LYP/LanL2DZ).

No	Reaction	$-E_{tot}$, a. u.		E_{C-H} *,
		Molecule/cat.	Anion/cat.	$\text{kJ}\cdot\text{mol}^{-1}$
a	<p>Charge= 1+ Charge= 0</p>	V_2O_5 : 883.4974	V_2O_5 : 883.0923	V_2O_5 : 1063.7
	Reaction	$-E_{tot}$, a. u.		DPE *,
		Molecule/cat.	Anion/cat.	$\text{kJ}\cdot\text{mol}^{-1}$
b	<p>Charge= 1+ Charge= 1+</p>	V_2O_5 : 883.4974	V_2O_5 : 883.4381	V_2O_5 : 155.7
c	<p>Charge= 1+ Charge= 1+</p>	V-Sn-O: 960.8955 V-Ti-O: 1015.7603	V-Sn-O: 960.8417 V-Ti-O: 1015.7081	V-Sn-O: 141.3 V-Ti-O: 137.0
d	<p>Charge= 1+ Charge= 1+</p>	V_2O_5 : 585.7023	V_2O_5 : 585.6400	V_2O_5 : 163.5

* E_{C-H} , DPE = $(E_{Anion/cat.} - E_{Molecule/cat.}) \times 2625.5$

The regularities of the influence of oxide modifiers revealed as a result of experiment and quantum chemical calculations allow creating a new catalyst for a more effective and "green" method of obtaining isonicotinic acid – a semi-product for the synthesis of various medical.

Nomenclature

A	Carbanion
AH	CH-acid
B	Proton acceptor
DPE	The enthalpy of a deprotonation
E _{C-H}	Energy of a heterolytic cleavage of methyl group C–H bond
E _{tot.}	The total energy of the corresponding compound
E(H ⁺)	Energy of proton formation
m	Multiplicity
PA	Proton affinity
q	Charge

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REFERENCES

- [1] Rubtsov M., Mikhlina E., Furshtatova B.J., Obtaining of Isonicotinic Acid, *Appl. Chem.*, **29**: 946–948 (1956). (in Russian)
- [2] Yugay O., Mikhailovskaya T., Sembaev D., Vorobyev P., Oxidation of 3- and 4-methylpyridines on Vanadia-Anatase and Vanadia-Rutile Catalysts, *Eur. Chem. Tech. J.*, **4**: 337–342 (2012).
- [3] Shishido T, Preparation of Crystalline CrVO₄ Catalyst by Soft Chemistry Technique and Application for Vapor-Phase Oxidation of Picolines, *J. Jap. Petrol. Inst.*, **54**(4): 225–236 (2011).
- [4] Suvorov B., Kagarlitskiy A., Afanasyeva T., Okislenie Organicheskikh Soedinenij. Soobshhenie XCIII. Parofaznoe Okislenie Nekotoryh 4-alkilpiridinov na Plavlenom Vanadievo-Titanovom Katalizatore, *Izvestiya AN KazSSR, Ser Chem (Chemical Bulletin of the Kazakh SSR Academy of Sciences)*, **1**: 51–55 (1974). [in Russian]
- [5] Shimanskaya M., Leitis L., Skolmeistere P., Yovel I., Golender L., "Vanadium Catalysts of Heterocyclic Compounds Oxidation", *Zinantne, Riga* (1990). [in Russian]
- [6] Bhattacharyya S.K., Kar A.K. Vapour Phase Oxidation of 4-Picoline to Isonicotinic Acid in Fluidized Bed, *Indian J. Appl. Chem.*, **30**: 42–47 (1967).
- [7] Bhattacharyya S.K., Shankar V., Kar A.K., Catalytic Vapor Phase Oxidation of monomethylpyridines to pyridinecarboxylic Acids, *Ind. Eng. Chem. Prod. Res. Dev.*, **5**(1): 65–72 (1966).
- [8] Martin A., Lücke B., Niclas H.-J., Förster A. Vapor-Phase Oxidation of 4-picoline to Pyridine-4-Carboxaldehyde on Vanadium Phosphate Catalyst, *React. Kinet. Catal. Lett.*, **43**(2): 583-588 (1991).
- [9] Kulkarni S.J., Ramachandra R.R., Subrahmayam M., Farsinavis S., Kanta R.P., Rama R.A.V., Oxidation and Ammoxidation of 4-picoline over Vanadium-Silico-Aluminophosphate Catalysts, *Ind. J. Chem. Sect. A*, **35**: 740–745 (1996).
- [10] Yang Gao-Jun, Huang Hai-Feng, Lu Han-Feng, Liu Hua-Yan, Chen Yin-Fei, Oxidation of 4-picoline to Isonicotinic Acid on V-Ti-O Catalysts, *J. Chem. Eng. Chinese U.*, **3**:448–453 (2007).
- [11] Hoelderich W., Verfahren Zur Herstellung von Isonikotinsaeure, *DE Patent 10146088* (2003).
- [12] Koch W., Holthausen M.C., "Chemist's Guide to Density Functional Theory", 2nd Ed., Wiley-VCH, Weinheim (2001).
- [13] Becke A.D., Density-Functional Thermochemistry. III. The Role of Exact Exchange, *J. Chem. Phys.*, **98**: 5648 (1993).
- [14] Lee C., Yang W., Parr R.G., Development of the Colle-Salvetti Correlation-Energy Formula Into a Functional of the Electron Density, *Phys. Rev. B*, **37**: 785 (1988).
- [15] Ganduglia-Pirovano M.V., Hofmann A., Sauer J., Oxygen Vacancies in Transition Metal and Rare Earth Oxides: Current State of Understanding and Remaining Challenge, *Surface Science Reports*, **62**: 219–270 (2007).
- [16] Sachtler W.M.H., Dorgelo G.J.H., Fahrenfort J., Voorhoeve R.J., Correlations between Catalytic and Thermodynamic Parameters of Transition Metal Oxides, *Rec. Trav. Chim.*, **89**: 460–480 (1970).
- [17] Yoshida S., Murakami T., Tarama K. 51:195 Structural Study on Promoting Actions of Titanium Dioxide and Stannic Oxide on Vanadium Pentoxide Catalysts, *Bull. Inst. Chem. Res., Kyoto Univ* , **51**(4): 195-205 (1973).

- [18] Sembaev D.Kh., Suvorov B.V., Saurambaeva L.I., Suleimanov Kh.T., O Svjazi Mezhdru Fazovym Sostavom i Kataliticheskim Dejstviem Okisnyh Vanadievo-Titanovyh Kontaktov v Reakcii Parofaznogo Okislenija o-Ksilola, *Kinetika i Kataliz (Russian Journal Kinetics and Catalysis)*, **20**: 750-755 (1979). [in Russian]
- [19] Sagitullin R S., Shkil' G P., Nosonova I.I., Ferber A.A., [Synthesis of Pyridine Bases by the Chichibabin Method \(Review\)](#), *Chem. Heterocycl. Compd.*, **32**(2):127–140 (1996)
- [20] Cram D.J., [“Fundamentals of Carbanion Chemistry”](#), Academic Press, New York–London (1965).
- [21] Witko M., Tokarz R., Haber J., [Quantum Chemical Calculations of Molecular Properties of V₂O₅ Clusters](#), *J. Mol. Catal.*, **66**(2): 205–214 (1991).
- [22] Witko M., Tokarz R., Haber J., [The Role of Atom Which Terminate Clusters: Quantum Chemical Study](#), *J. Mol. Catal.*, **66**(3): 357–366 (1991).