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P. B. VOROBYEV[1], T. P. MIKHAILOVSKAYA[1], A. M. IMANGAZY[2]

[1]«A.B. Bekturov Institute of Chemical Sciences» JSC, Almaty, Kazakhstan,
[2]Satbayev University, Almaty, Kazakhstan

THE ROLE OF QUANTUM CHEMISTRY IN THE STUDY OF MECHANISM OF CATALYTIC OXIDATION AND OXIDATIVE AMMONOLYSIS REACTIONS

Abstract. The role of quantum chemistry in the study of the reactivity and mechanism of catalytic oxidation and oxidative ammonolysis of methylaromatic compounds is discussed. The new approach based on a combination of experimental kinetic researches and quantum-chemical modeling of the active centers of vanadium oxide catalysts and their chemisorption interaction with methylpyridine molecules and the most likely products of their transformations has been developed in ICS. Application of this approach allowed to put forward hypotheses about the nature of such peculiar phenomena for catalisys, as promotion, energy compensation and synergistic effect.

Keywords: quantum chemistry, methylpyridines, reactivity, oxidation, oxidative ammonolysis, catalysts, mechanism.

Modern physical methods (spectroscopy of adsorbed molecules, slow electron diffraction, photoelectron spectroscopy, etc.) have provided catalysis with the possibility of obtaining valuable information about the patterns of reactions on the surface of a catalyst, its state, and changes under the influence of the reaction medium [1-5]. However, none of these methods gives reasons for unambiguous conclusions about the mechanism obtained only with its help. This limitation is caused, in particular, by the fact that often the conditions of physical studies do not correspond to the conditions of catalysis, and the intermediates found in isolation from kinetic studies can be dead ends, by-products and not be responsible for the course of the main catalytic reaction. This leads to the conclusion that in order to identify the true mechanism of the catalytic reaction, a combination of kinetic and other physicochemical studies is necessary. There are very few examples of such complex studies in the literature. At «A.B. Bekturov Institute of Chemical Sciences» JSC [6] to study the mechanism of catalytic oxidation and oxidative ammonolysis of methylaromatic compounds, a new approach was proposed based on a combination of experimental kinetic studies and quantum-chemical modeling of the active centers of vanadium oxide catalysts and their chemisorption interac-tion with methylpyridine molecules and the most likely products of their transformations. The development of high-performance computers and the emergence of new methods of quantum chemical calculations opened up great opportunities in this area.

At the first stages of the studies of catalytic oxidation and oxidative ammonolysis of methyl aromatic compounds [7, 8], it was assumed that these processes proceed similarly to homogeneous oxidation, the mechanism of which is most reliably described by A.N. Bakh [9] and the theory of radical chain processes with degenerate branches developed by N.N. Semenov [10]. This was facilitated by the fact that the homogeneous and heterogeneous catalytic oxidation of certain hydrocarbons produced the same products. For these processes, schemes were discussed in detail in which free radicals were considered as intermediate forms. However, later by the EPR method, hydrocarbon or peroxide radicals were not detected on the surface of the catalysts during oxidation [11]. The hypothesis of a reaction mechanism with a homolytic cleavage of the C-H bond in an oxidizable methyl substituent is also evidenced by the absence of a correlation between the reaction rate and the homolytic cleavage energy of this bond. Thus, according to reference data [12], the experimental values of the energy of homolytic rupture ($E_{C\text{-}H}$, $kJ{\cdot}mol^{-1}$) grow in the order: 2-methylpyridine (314) <3-methylpyridine (318) < 4-methylpyridine (322) and do not correlate with their relative reactivity under conditions of catalytic oxidation and oxidative ammonolysis (3-methylpyridine <2-methylpyridine < 4-methylpyridine).

The transformation of views on the mechanism of the initial stages of catalytic oxidation and oxidative ammonolysis occurred with the development of ideas about organic CH-acids [13-17], the development of a theory of adsorption and catalysis on the surface of transition metal oxides, the development of physical methods for the experimental study of intermediate surface compounds during the catalytic reaction [1-5]. Numerous studies have shown the important role of acid-base and redox properties of the surface of oxide catalysts, in particular, the role of various forms of oxygen and its binding energy to the surface of the catalyst in the formation of activity and selectivity of the catalyst.

Theoretical ideas about acids and bases, together with the results of kinetic experiments and quantum-chemical studies of the reactivity of methylpyridines at the Institute of Chemical Sciences, contributed to the formation of new views on the mechanism of catalytic reactions of oxidation and oxidative ammonolysis. They are based on the hypothesis of heterolytic cleavage of the C-H bond in the methyl group at the initial stages of the processes [6, 18, 19].

Since there are no experimental data on acid-base characteristics in the gas phase for most of the starting materials, we calculated their analogs using non-empirical (*ab initio*) quantum-chemical methods [20]. Chemisorption of initial materials on the surface of vanadium oxide catalysts was simulated using the cluster approximation, which is currently widely used to study the mechanism of heterogeneous catalytic reactions [21, 22]. Clusters and their complexes with substrates and products of their primary transformation (in our case, carbanions) were calculated using the density functional theory (DFT, Density Functional Theory) [23].

The electronic structure of pyridine resembles benzene [24]. All carbon and nitrogen atoms are in a sp^2 hybridization state, and all σ bonds (C–C, C–N, and C–H) lie in the same plane. Of the three hybrid orbitals of the nitrogen atom, two are involved in the formation of σ bonds with carbon atoms, and the third orbital contains an unshared pair of electrons and is not involved in the formation of bonds. A nitrogen atom with such an electronic configuration is called pyridine.

Due to the electron located on the non-hybridized *p*-orbitals, the nitrogen atom participates in the formation of a single electron cloud with *p*-electrons of five carbon atoms. Thus, pyridine is a π,π-conjugated system and satisfies the criteria of aromaticity [25]. As a result of higher electronegativity compared to the carbon atom, the pyridine nitrogen atom lowers the electron density on the carbon atoms of the aromatic ring, and therefore systems with the pyridine nitrogen atom are called π-deficient. In pyridine, the lone pair of electrons of the nitrogen atom does not take part in the formation of the π-electron sextet and is responsible for the manifestation of its basic properties.

The introduction of a methyl substituent into the pyridine ring substantially changes the nature of the compound, making it bifunctional. Remaining a base due to the presence of a nitrogen heteroatom, the compound acquires the properties of a CH-acid, capable of cleaving a proton from a methyl group under the action of a nucleophile, which has a fairly high proton affinity. The use of non-empirical quantum-chemical calculations with chemical accuracy [20] allows us to quantitatively evaluate the basicity and CH-acidity of the studied compounds.

The basicity of the initial methylpyridines (B) was calculated as the proton affinity (PA) based on the total energies of the initial molecules and their nitrogen-protonated ring forms with optimized geometry. We used the non-empirical quantum-chemical method (ab initio) with the Pople basis sets HF/6-311 + G(2d,2p), including two *d*-functions of non-hydrogen atoms (plus diffuse functions) and two *p*-functions of hydrogens:

$$B + H^+ = BH^+ + PA \qquad (1)$$

$$PA = E_{total}(B) + E_{total}(H^+) - E_{total}(BH^+) \qquad (2)$$

The total energy of the proton is a constant, and to compare the relative basicity of the initial compounds, you can use the equation:

$$PA = E_{total}(B) - E_{total}(BH^+) \qquad (3)$$

Thus, the basicity of pyridine and its methyl derivatives is estimated by proton affinity, i.e. the amount of energy released as a result of the attachment of a proton to a nitrogen heteroatom and the formation of a new N–H bond due to its lone electron pair.

An interesting fact should be noted that the introduction of an electron-donating methyl substituent in the pyridine ring leads to an increase in basicity (proton affinity). Presumably, this effect is associated with a decrease in the degree of delocalization of the lone electron pair of the nitrogen atom, which in turn leads to an increase in its ability to interact with the Lewis and Bronsted acid centers of the catalyst surface. Methyl substituents at the 2- and 4-positions of the pyridine ring have the highest influence on the basicity due to the conjugation effect, and in the case of the 4-methyl group this effect is enhanced by «hyperconjugation» due to the aromaticity of the pyridine ring [24, 25]. The impact of the methyl substituent in position 3 on the basicity is much less, since it is associated with the manifestation of a weaker inductive effect.

The adsorption interaction of methylpyridines with a nitrogen atom and acid sites of the catalyst makes a significant contribution to the activation of methyl groups, which entails the transfer of the reaction center from the nitrogen atom of the ring to the methyl group. Despite the existing experimental methods for determining the basicity of organic compounds in the gas phase (high pressure mass spectrometry, ion-cyclotron resonance spectroscopy) [14], the information on this issue is far from complete. Therefore, we calculated the basicity values of isomeric methylpyridines as proton affinity (PA in equation 3).

The calculated proton affinity characterizing the basicity, calculated by the *ab initio* method [HF/6-311+G (2d, 2p)], is provided in table 1. It was established that the basicity of isomeric methylpyridines in the gas phase (PA, kJ·mol^{-1}) increases in the order:

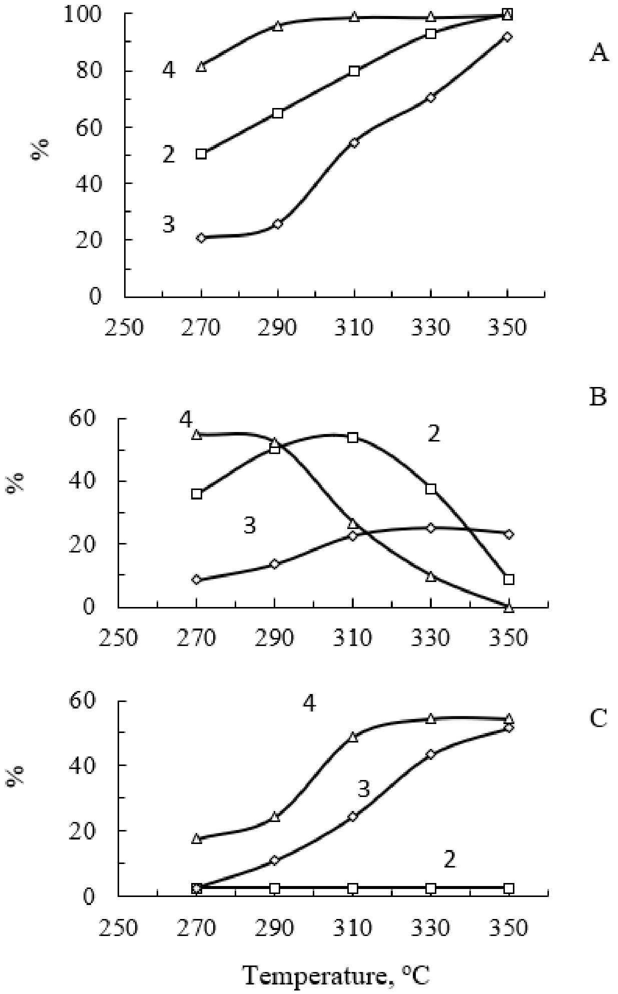
3-methylpyridine (995.9) < 2-methylpyridine (1002.4) <
< 4-methylpyridine (1003.2)

Table 1 – The total energies of the bases, protonated by nitrogen ring form (E_{total}), the proton affinity (PA), calculated by the *ab initio* method [HF/6-311+G(2d,2p)]

№	Compound	– $E_{total.}$, a.u.		PA*, kJ·mol^{-1}
		isolated molecules (M)	protonated nitrogen rings form (MH$^+$)	
1	Pyridine	246.7650	247.1397	983.7
2	3-methylpyridine	285.8130	286.1923	995.9
3	2-methylpyridine	285.8171	286.1989	1002.4
4	4-methylpyridine	285.8152	286.1973	1003.2
Note: * PA= (E_M -E_{MH+})·2625.46.				

In the same series, the reactivity of methylpyridines in the process of catalytic oxidation increases, estimated by the degree of conversion and the yield of partial oxidation products (figure 1). In the case of 2-methylpyridine, the low yield of picolinic acid is explained by its tendency to decarboxylation under conditions of vapor-phase catalytic oxidation.

The introduction of a methyl substituent into the pyridine ring leads to the appearance of a new property and makes these compounds bifunctional. It is known that methyl pyridines are among weak CH acids [13–16] and, under the action of a strong base, are able to cleave the proton from the methyl group, for example, in liquid phase deuterium exchange [17]. This reaction proceeds with the formation of carbanion. The coincidence of the sequence of changes in the reactivity of methylpyridines during deuterium exchange and in oxidation and oxidative ammonolysis suggests that the activation of picolines methyl groups under the conditions of a heterogeneous catalytic reaction proceeds according to a similar mechanism with heterolytic cleavage of the C–H bond. In the catalytic reaction, the role of



Speed of submission methyl pyridines 36 $g \cdot l^{-1} \cdot h^{-1}$,
molar the relation initial substance:O_2:H_2O=1:15:113. A designation of curves (substance):
2 - 2-methylpyridine, 3 - 3-methylpyridine, 4 - 4-methylpyridine.

Figure 1 – Influence of temperature on conversion methyl pyridines (A),
an yields of pyridine-aldehydes (B) and pyridine-carboxylic acids (C)
in conditions of oxidation on V-Ti-Al-O the catalyst

proton acceptors can be played by various forms of surface oxygen bound to vanadium atoms [11]. Obviously, the rate of deprotonation of methyl substituents converted to carboxy- or cyano-groups should influence the reaction rate. The data on the experimental values of CH acidity of methylaromatic molecules are not completely presented in the literature; therefore, using the non-empirical quantum-chemical ab initio method using the Pople basis sets [HF/6-311+G(2d,2p)], we calculated values methyl group deprotonation enthalpies (DPE, Deprotonation Enthalpy) as analogues of CH acidity of methylpyridine molecules.

The equation for the reaction of CH-acid with a proton acceptor is:

$$AH + B = A^{-} + BH^{+} – DPE \quad (4)$$

$$DPE = E_{total}(A^{-}) + E_{total}(BH^{+}) – E_{total}(AH) – E_{total}(B) \quad (5)$$

where E_{total} is the total energy of the corresponding compound, B is the main center, the proton acceptor. For the same proton acceptor, the difference E_{total} (BH +) - E_{total} (B) in equation (5), equal to the proton binding energy, can be considered constant. Therefore, to calculate the deprotonation enthalpy that characterizes the relative strength of CH acids, one can use an equation that includes the total energies of the carbon anions and the initial molecules with optimized geometry:

$$DPE = E_{total}(A^{-}) – E_{total}(AH) \quad (6)$$

According to the results of quantum-chemical calculations using the Pople basis sets [HF/6-311+G (2d, 2p)] (table 2), the CH-acidity of isomeric methylpyridines in the gas phase increases as the deprotonation of methyl groups (DPE, $kJ{\cdot}mol^{-1}$) in a row:

3-methylpyridine < 2-methylpyridine < 4-methylpyridine

Table 2 – The total energies of the molecules of isomeric methylpyridines and the corresponding anions (E_{total}), the enthalpies of proton detachment from methyl groups in the gas phase (DPE), the energies of the higher occupied molecular orbitals of anions (E_{HOMO}), calculated by the *ab initio* method [HF/6-311+G (2d,2p)]

№	Initial compound	$-E_{total}$, a.u.		DPE*, $KJ{\cdot}mol^{-1}$	$-E_{HOMO}$, $KJ{\cdot}mol^{-1}$
		molecules	anions		
1	3-methylpyridine	285.8130	285.1766	1670.8	87.1
2	2-methylpyridine	285.8171	285.1868	1654.9	116.4
3	4-methylpyridine	285.8152	285.1958	1626	148.1

Note: *DPE = [E_{total}(anion) –E_{total}(molecule)] · 2625.46.

While discussing the relationship between the structure and reactivity of methylpyridines, it is necessary to take into account the fact that, due to the peculiarities of their structure, they are bifunctional compounds. On the one hand, as mentioned above, the presence of an electron-withdrawing nitrogen atom in the cycle provides a qualitative difference between pyridine derivatives and methylbenzenes, giving them a higher basicity [24]. On the other hand, methylpyridines are among the weak CH acids and are capable of cleaving the proton from the methyl group. This structural feature of methylpyridines must be correlated with the surface properties of vanadium oxide catalysts, which contains both the Bronsted acid centers (surface proton donor hydroxyl groups) and Lewis (electron-withdrawing valence-unsaturated metal cations) capable of interacting with a lone electron pair of nitrogen heteroatom and various vanadium bound oxygen species [11], responsible for the deprotonation of oxidizing methyl substituents.

Table 2 also gives the calculated energies of the highest occupied molecular orbitals of intermediate carbanions (E_{HOMO}, $kJ \cdot mol^{-1}$), which characterize their stability[24]. The lone electron pair of the carbonation is located on the highest filled molecular orbital (HOMO). The more the lone electron pair is delocalized (i.e., the more its electron density is shifted toward the ring), the lower the energy of the HOMO (energy has a more negative value) and, therefore, the more stable the carbanion. The more stable the carbanion, the higher the probability that it will not capture the proton back, but will turn into the final reaction product (aldehyde, acid or nitrile).

According to the table 2, the methyl group of 4-picoline gives off a proton more easily, and the resulting carbanion is more stable than the 2- and 3-isomers; therefore, the conversion rate of 4-picoline to partial oxidation products is higher (figures 1 and 2).

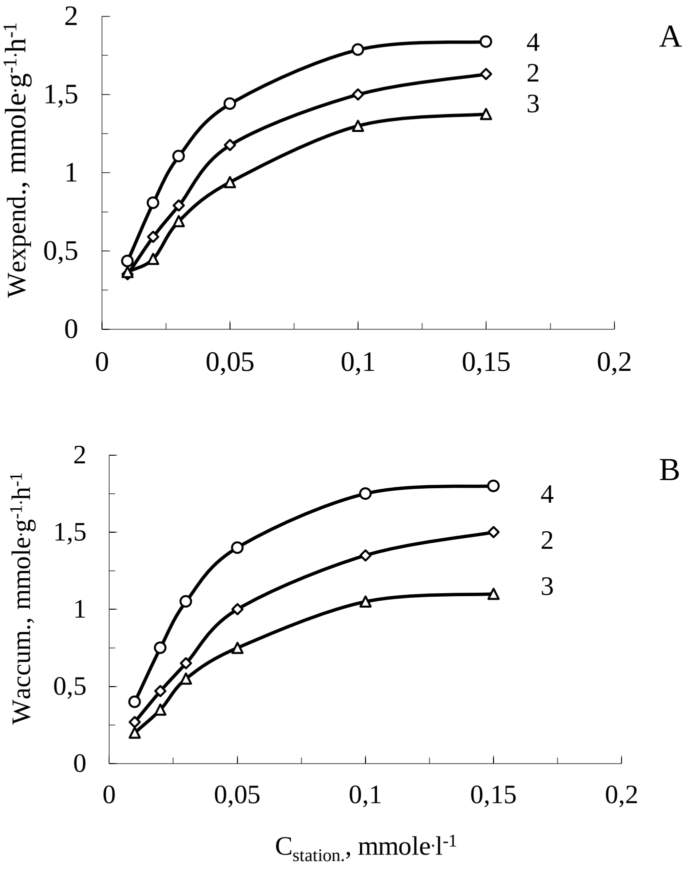
Pyridinecarboxylic acids and their derivatives have various physiological properties and are widely used in medicine and agriculture. Therefore, the promotion of vanadium pentoxide by additives of various oxides plays an important role in increasing the productivity of their synthesis processes.

Our studies of the 3- and 4-methylpyridines oxidation over a catalyst from individual V_2O_5 and over binary vanadium oxide catalysts obtained by its modification showed that additives of modifying oxides have a promoting effect on the catalytic properties of two-component contacts. The **promotion effect** is appeared in an increase in the conversion of the initial methylpyridines, an increase in the yield of the target products, and a decrease in the optimal reaction temperature for their obtaining.

Among the carboxylic acids of the pyridine series, nicotinic acid occupies an important place, on the basis of which Cordiamine, Feramide, Nicodan, Ethiacin, Vitamin PP and other therapeutic preparations are obtained [26]. Niacin is also used in the manufacture of premixes in animal husbandry. The preparation of nicotinic acid is currently based on the liquid-phase oxidation of 3-methylpyridine with inorganic oxidizing agents or the hydrolysis of nicotinic acid nitrile formed during the oxidative ammonolysis of the initial methylpyridine [27].

We studied the catalytic properties of a number of catalysts containing V_2O_5 and Ti, Sn, Zr, Nb and Al oxides in the vapor-phase oxidation of 3-methylpyridine into nicotinic acid. It was established a relationship between the catalytic activity of the synthesized binary oxide catalysts and proton affinity calculated by quantum-chemical methods (nucleophilicity) of active oxygen bound to vanadium [18].

We interpreted the obtained experimental data using quantum chemical calculations, according to which titanium, tin, and zirconium dioxide, niobium pentoxide, and alumina (III), when added to vanadium pentoxide, can increase the proton affinity of vanadium-bound active oxygen, which is involved in the deprotonation of oxidized methyl 3-methylpyridine groups (figure 3).



Volumetric speed 6000 h^{-1}. The initial concentration of oxygen 4.2, ammonia 1.7 mol·l^{-1}. Temperature 390°C. Curve designation (initial material and products): 2 - 2-methylpyridine and picolinonitrile, 3 - 3-methylpyridine and nicotinonitrile, 4 - 4-methylpyridine and isonicotinonitrile.
Figure 2 – The effect of a stationary concentration of isomeric methylpyridines ($C_{station.}$) on their expenditure rate (A) and nitrile accumulation (B) under conditions of oxidative ammonolysis over V_2O_5 catalyst

It was found that the modification of V_2O_5 with Ti, Sn, Zr, Nb, and Al oxides leads to an increase in the activity and selectivity of the vanadium oxide catalyst in the vapor-phase oxidation of 3-methylpyridine to nicotinic acid. It was shown that over two-component V_2O_5-TiO_2, V_2O_5-SnO_2, V_2O_5-ZrO_2, V_2O_5-Nb_2O_5 and V_2O_5-Al_2O_3catalysts, the conversion of 3-methylpyridine and the yield of nicotinic acid can be several times higher than the same indices on the catalyst from V_2O_5. It was established that, when passing from V_2O_5 to two-component vanadium-containing catalysts, simultaneously with an increase in the values of the proton affinity calculated by the quantum-chemical method for active oxygen bound to vanadium (figure 3), the activity of contacts in the oxidation reaction increases [18].

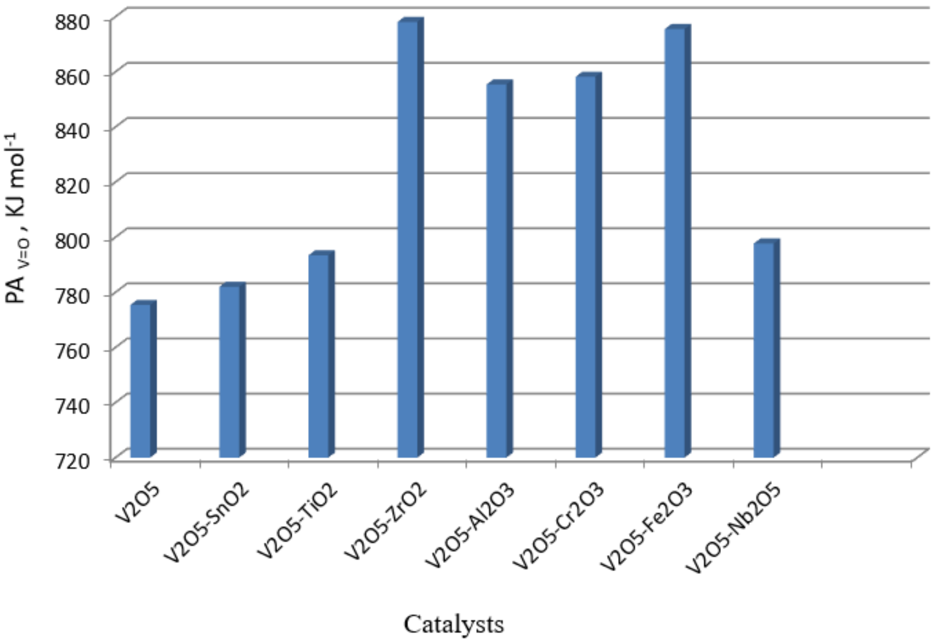


Figure 3 – The effect of modifiers on the proton affinity of vanadyl oxygen, calculated by Single Point using an extended basis (for the metal atoms, the Studgardt two-exponential SSD set was used, for the other atoms, the basic set HF/6-31++G(d,p) was used, including polarization and diffuse functions). The geometry of the structures was previously optimized by the DFT method (B3LYP/LanL2DZ). Calculations using the G09W program

The active sites of the catalysts were modeled by clusters [21, 22] containing fragments of V_2O_5 and promoter oxides. Based on the obtained results, it can be concluded that the observed effect of the studied additives on the activity and selectivity of binary catalysts is associated with a change in their degree of nucleophilicity of vanadyl oxygen [11], which is involved in the deprotonation of an oxidizable methyl substituent.

The development of heterogeneous catalytic processes for the oxidation of 4-methylpyridine to isonicotinic acid, which is currently underway at «A.B. Bekturov Institute of Chemical Sciences» JSC, is aimed at developing new, more effective, environmentally friendly and safe methods for producing anti-tuberculosis drugs based on it [26].

In the oxidation of 4-methylpyridine on a fused catalyst of composition V_2O_5:TiO_2 = 1: 0.5, depending on the conditions, pyridine-4-aldehyde (yield 70–72%) or isonicotinic acid (yield 55–57%). It was noted that a decrease in the concentration of water vapor in the reaction mixture contributes to an increase in the yield of pyridine-4-aldehyde [28].

We studied the partial oxidation of 4-methylpyridine under comparable conditions on binary and ternary vanadium oxide catalysts promoted by additions of titanium, aluminum, iron, and zirconium oxides, and also established the influence of the nature of the promoter oxide and reaction conditions on the selectivity of the oxidation process [18].

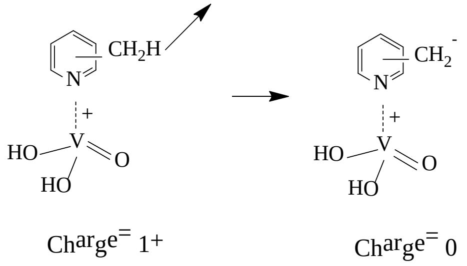
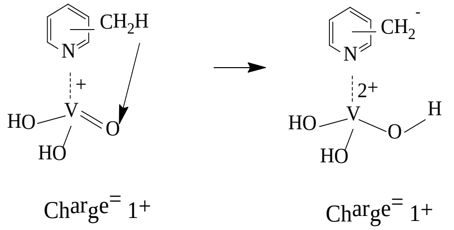
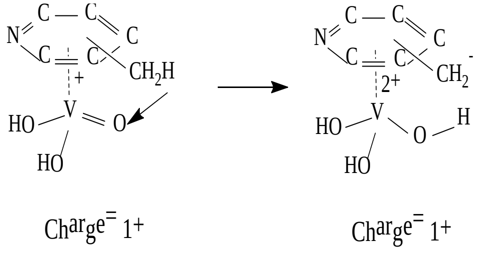
It was established that the nature of the modifier oxide has a noticeable effect on the selectivity of binary catalysts in the oxidation of 4-methylpyridine under the conditions studied. Over V-Ti- and V-Zr-oxide catalysts, the only partial oxidation product is isonicotinic acid, which is formed in low-temperature experiments with a selectivity of 85–98%. During the oxidation of 4-methylpyridine on catalysts made from individual vanadium (V) oxide and binary V–Al and V–Fe oxide catalysts, pyridine-4-carbaldehyde is found to be appreciable in addition to isonicotinic acid in the reaction products. The selectivity of the formation of isonicotinic acid on all the studied modified catalystsis higher than on the catalyst from individual vanadium (V) oxide. The nucleophilicity of vanadyl oxygen, calculated by us as the proton affinity for the binary catalysts, using an extended basis is also higher (the Studgardt two-exponential SSD set was used for metal atoms, and the basic set 6-31++G(d,p) was used for other atoms including polarization and diffuse functions) (figure 3).

The partial oxidation of 4-methylpyridine to V_2O_5 and binary vanadium oxide catalysts promoted by TiO_2, Al_2O_3, Fe_2O_3 and ZrO_2 additives was studied. The catalytic activity of the studied contacts and the calculated values of the proton affinity of vanadyl oxygen are compared (figure 3). It was suggested that the mechanism of individual vanadium pentoxide promotion by the listed oxides consists in increasing under their influence the nucleophilicity of vanadyl oxygen, which is responsible for the deprotonation of the oxidized methyl group of the substrate at the initial stages of the oxidation process.

We carried out the quantum-chemical modeling of the chemisorption of isomeric methylpyridines (MP) on the surface of a vanadium oxide catalyst with the transfer of a methyl group proton to vanadyl oxygen. The active center of the catalyst was modeled by a minimal cluster with one vanadium atom (table 3), as well as a two-core cluster containing the Lewis acid center (V^{4+} ion) and vanadyl oxygen (table 4).

The energy of heterolytic cleavage of the C–H bond in the methyl substituent was calculated from the difference in the total energies of the chemisorbed carbon anion and the molecule. Moreover, it was assumed that the proton detached from the methyl group is transferred «to infinity», and the charge of the carbonanion/cluster complex changes from 1+ to zero. As can be seen from the table3, the energy of heterolytic cleavage of the C–H bond in the methyl groups of chemisorbed substrates reaches significant values (more than 1000 $kJ{\cdot}mol^{-1}$). At the same time, it is known that the experimentally determined activation energy of such reactions is 80–100 $kJ{\cdot}mol^{-1}$. It must be assumed that a decrease in the energy barrier under conditions of heterogeneous catalysis occurs, according to the views of academician G.K. Boreskov [29], as a result of the compensation of a part of the energy required for heterolytic breaking of the C–H bond of the methyl group due to the energy released as a result of the addition of a proton to vanadyl oxygen with the formation of a new V–O–H bond. Calculations showed that the values of the deprotonation enthalpy of the methyl group [DPE (ads.), kJ mol^{-1}] are of the same order as the experimental activation energies and decrease in the order 3-MP/cluster (238.5) <2-MP/cluster (239.3) <4-MP/cluster (163.5). According to the results of the experiment, under the conditions of catalytic oxidation, the conversion of the initial methylpyridines and the yield of partial oxidation products naturally increase in the same series with a decrease in the deprotonation enthalpy of methyl groups (figure 2).

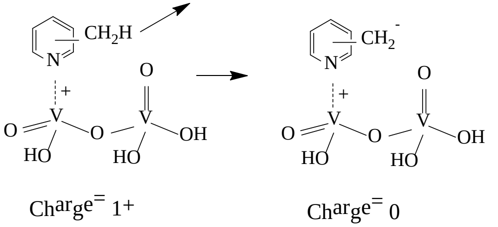
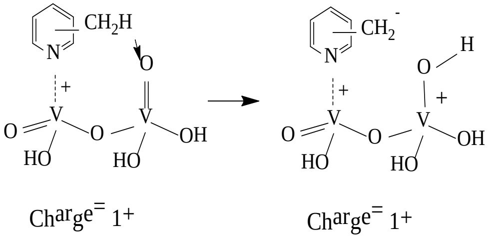
Table 3 – Total energies of methylpyridines and their carbanions (E_{total}) associated with the mononuclear Lewis acid center of the vanadium oxide catalyst (E_{total}), C–H bond heterolytic energy (E_{C-H}) and methyl group deprotonation enthalpy with energy compensation due to proton transfer to vanadyl oxygen (DPE) calculated by the DFT method (B3LYP/LanL2DZ)

Reaction without energy compensation	$-E_{total}$, a.u.		E_{C-H}*, kJ·mol^{-1}
	Chemisorbed molecule	Chemisorbed Carbanion	
	585.6995 (3) 585.6989 (2) 585.7023 (4)	585.2514 (3) 585.28824 (2) 585.2981 (4)	1176.6 (3) 1078.2 (2) 1061.3 (4)
Energy Compensated Reaction	$-E_{total}$, a.u.		DPE*, kJ·mol^{-1}
	Chemisorbed molecule	Chemisorbed Carbanion	
	585.6995 (3) 585.6989 (2) 585.7023 (4)	585.6084 (3) 585.6323 (2) 585.6400 (4)	239.3 (3) 174.8 (2) 163.5 (4)
	585.6995 (3) 585.6989 (2) 585.7023 (4)	585.6084 (3) 585.6327(2) 585.6400 (4)	239.4 (3) 173.9 (2) 163.5 (4)
Note: *E_{C-H}, DPE = ($E_{anion/cluster}$ − $E_{molecule/cluster}$) · 2625.46.			

The sequence of changes in reactivity in the series of isomeric methylpyridines is also maintained under conditions of oxidative ammonolysis. According to the figure 3 results, in the studied range of stationary concentrations of methylpyridines, the rates of their expenditure and accumulation of cyanopyridines increase in the series: 3-methylpyridine <2-methylpyridine < 4-methylpyridine.

In favor of the correctness of our use, for modeling the chemisorption of methylpyridines, of a minimal surface cluster (with one vanadium atom), the fact that, while passing to a more extended cluster with two vanadium atoms, the results of calculations of the energy of heterolytic C–H bond cleavage in methyl groups ($E_{C\text{-}H}$) and their deprotonation enthalpies (DPE) with proton transfer to vanadyl oxygen are practically unchanged (table 4).

Table 4 – The total energies of methylpyridines and their carbanions associated with the binuclear cluster (E_{total}), the deprotonation enthalpies of methyl substituents (DPE) calculated by the DFT method (B3LYP/LanL2DZ)

Reaction without energy compensation	$-E_{total}$, a.u.		$E_{C\text{-}H}$*, kJ·mol^{-1}
	Chemisorbed molecule	Chemisorbed Carbanion	
	883.4949 (3) 883.4969 (2) 883.4975 (4)	883.0492 (3) 883.0834 (2) 883.0923 (4)	1170.1 (3) 1085.5 (2) 1063.7 (4)
Deprotonation of the CH_3 substituent with proton transfer to vanadyl oxygen	$-E_{total}$, a.u.		DPE*, kJ·mol^{-1}
	Chemisorbed molecule	Chemisorbed Carbanion	
	883.4949 (3) 883.4969 (2) 883.4975 (4)	883.4040 (3) 883.4297 (2) 883.4382 (4)	238.5 (3) 176.3 (2) 155.7 (4)
Note: * $E_{C\text{-}H}$, DPE = ($E_{anion/cluster} - E_{molecule/cluster}$) ·2625,5.			

Thus, as a result of experimental and theoretical studies, a correlation between the basicity and acidity of isomeric methylpyridines in the gas phase and their relative reactivity under conditions of gas-phase catalytic oxidation (figure 1) and oxidative ammonolysis (figure 2)was found, which is in favor the staged mechanism of these reactions with heterolytic cleavage of the C–H bond in oxidizable methyl groups and the intermediate formation of carbanions. The reactivity of isomeric methylpyridines in oxidation and oxidative ammonolysis, estimated by the rate of substrate expenditure and accumulation of the corresponding pyridine carboxylic acids and their nitriles, increases in the order: 3-methylpyridine <2-methylpyridine <4-methylpyridineand correlates with the enthalpy of deprotonation of the methyl substituent in the gas phase.

The first act of the catalytic process, of course, is their chemisorption on the contact surface. Of great theoretical and practical interest is the mechanism of interaction of methylpyridines with active centers of the surface of the vanadium oxide catalyst. According to [11], the surface of vanadium oxide catalysts contains Lewis acid sites (vanadium cations), on which methylpyridines can be adsorbed, as well as various forms of oxygen, which are responsible for the detachment of the proton from the oxidizing methyl group at the initial stages of the process. The active centers of the surface were modeled by clusters representing a fragment of the surface containing one or two vanadium atoms surrounded by oxygen atoms.

To simulate the chemisorption of the initial compounds and the primary products of their transformation (carbon anions) on the surface of the oxide catalyst, the density functional method (DFT, Density Functional Theory) was used [23]. To optimize the geometry and calculate the total energy of the complexes, we used the B3LYP exchange-correlation density functional method and the Lanl2DZ two-exponential basis set with an effective core potential. At the first stage, the energies of the heterolytic bond cleavage of C–H methyl groups ($E_{C–H}$) were estimated by the difference in the total energies of the complexes of the starting compounds and the corresponding carbon anions with optimized geometry. It was found that the rates of expenditure of the initial compounds and the accumulation of pyridine carboxylic acids and their nitriles under conditions of oxidation and oxidative ammonolysis increase with decreasing $E_{C–H}$ (kJ·mol^{-1}) methyl groups of substrates associated with the cluster in the order: 3-methylpyridine (1176.6) - 2-methylpyridine (1078.2) – 4-methylpyridine (1063.7) (Table 3). Attention should be given to the high values of the heterolytic cleavage energy of the C–H bond of methyl groups.

According to academician Boreskov G.K. [29], an increase in the rate of heterogeneous catalytic reactions proceeding according to a separate mechanism is possible due to an increase in the degree of **energy compensation** of old bonds breaking due to the energy released at the stage of formation of new bonds. In our case, we are talking about lowering the high energy barrier at the stage of heterolytic breaking of the C–H bond in the oxidizable methyl group due to the energy released during the formation of a new V–O–H bond as a result of the addition of the proton detached from the methyl group to vanadyl oxygen. A similar compensation effect was demonstrated by the results of our calculations with simulation of proton transfer from a methyl group to vanadyl oxygen (table 3).

It is characteristic that the experimentally established reactivity of the substrates increases as the calculated DPE values of the «adsorbed» substrates (kJ·mol^{-1}) decrease in the series: 3-MP/cluster (239.3) – 2-MP/cluster (174.8) – 4-MP/cluster (163.5).

Calculations for complexes with planar adsorption of methylpyridines and their carbanions at the Lewis acid center led to almost the same DPE values (table 3).

Visualization of the results of quantum chemical calculations showed that in the process of optimizing the geometry of complexes with a planar arrangement of the molecule (anion), they are converted into complexes with vertically arranged molecules connected by a ring nitrogen atom to the vanadium cation. This can be explained by the fact that this type of adsorption is energetically more profitable. After activation of the molecule, the reaction center is transferred from the nitrogen atom to the methyl substituent.

As an experimental confirmation of the possibility and preference of «vertical» adsorption, one can refer to an article whose authors, using X-ray absorption spectroscopy (XAS) and scanning tunneling microscopy (STM), showed that during the adsorption of isomeric pyridine monocarboxylic acids on the surface of rutile TiO_2 (110) pyridine rings oriented so that their planes are mainly perpendicular to the surface [30].

Table 5 shows the rate constants of the stage of cyanopyridines formation (k_j) at 390ºC, obtained by mathematical processing of the experimental kinetic data shown in figure 3. As can be seen from the table 5, the rate constants increase in the series 3-methylpyridine <2-methylpyridine <4-methylpyridine, as the basicity of the substrates (PA) increases and the enthalpy of deprotonation of their methyl groups in the gas phase decreases [DPE (gas)] and under conditions simulating chemisorption on catalyst surface [DPE (ads)].

Table 5 – Proton Affinity of methylpyridines in the gas phase (PA), the enthalpy of deprotonation of methyl substituents in the gas phase [DPE (gas)] and under conditions simulating chemisorption [DPE (ads)], the rate constants of the stage of cyanopyridines formation under conditions of oxidative ammonolysis on vanadium oxide catalyst at 390ºC (k_i)

Compounds	PA, $kJ \cdot mol^{-1}$	DPE (gas), $kJ \cdot mol^{-1}$	DPE (ads), $kJ \cdot mol^{-1}$	k_i, $L \cdot g^{-1} \cdot h^{-1}$
3-methylpyridine	995.9	1670.8	238.5	0.9883
2-methylpyridine	1002.4	1654.9	176.3	6.0746
4-methylpyridine	1003.2	1626	155.7	12.438

Thus, the results of quantum chemical calculations of the enthalpy of proton separation from methyl substituents of the studied compounds under conditions simulating chemisorption on the surface of a vanadium oxide catalyst correctly reflect the patterns of relative reactivity of methyl groups of the initial compounds under conditions of catalytic oxidation and oxidative ammonolysis.

The approach developed at the Institute of Chemical Sciences to study the mechanism of catalytic oxidation and oxidative ammonolysis of methylpyridines [6] differs from the literature [1-5] in that experimental data on relative catalytic activity are interpreted using the results of quantum-chemical modeling of chemisorption of substrates on active centers of the surface of vanadium oxide catalysts, as well as the processes of promotion of vanadium pentoxide by additives of oxides of various nature.

The application of the new approach allowed us to hypothesize the nature of the **synergistic effect** [31], which is observed with the simultaneous modification of vanadium pentoxide by the addition of two oxides: titanium (IV) and tin (IV), titanium (IV) and zirconium (IV), titanium (IV) and chromium (III), and manifests itself in a noticeable increase in catalytic activity during the transition from individual vanadium pentoxide and binary oxide systems to ternary contacts [32-38]. In the same series of catalysts, an increase in the calculated proton affinity of vanadyl oxygen in three-component catalysts was observed (figure 4).

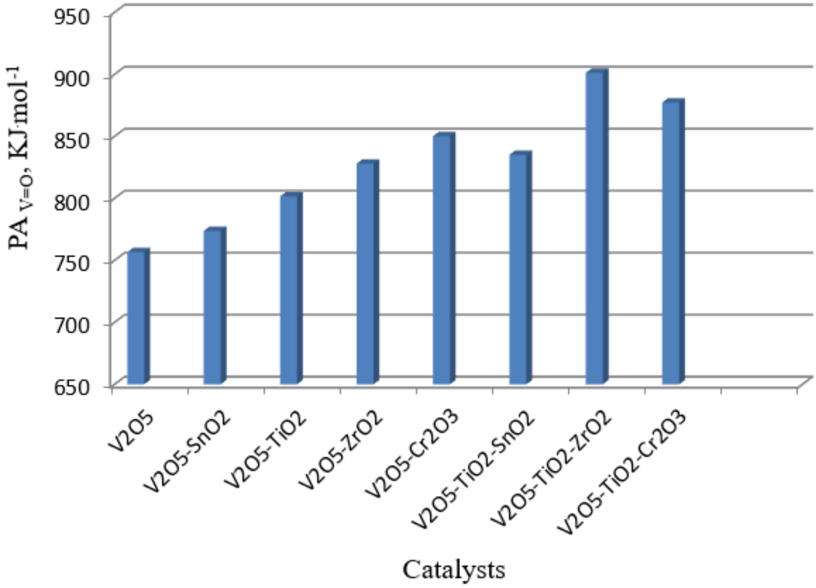


Figure 4 – The proton affinity of vanadyl oxygen V_2O_5, binary and ternary catalysts.
DFT calculations (B3LYP/LanL2DZ)

Conclusion. For revealing the true mechanism of the catalytic reaction, a combination of kinetic and other physicochemical studies is necessary. There are very few examples of such complex studies in the literature. To study the mechanism of catalytic oxidation and oxidative ammonolysis of methylaromatic compounds, a new approach based on a combination of experimental kinetic studies and quantum-chemical modeling of the active centers of vanadium oxide catalysts and their chemisorption interaction with methylpyridine molecules and the most likely products of their transformations was proposed at «A.B. Bekturov Institute of Chemical Sciences» JSC. The development of high-performance computers and the emergence of new methods of quantum chemical calculations opened up great opportunities in this area.

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Резюме

П. Б. Воробьев, Т. П. Михайловская, А. М. Иманғазы

КАТАЛИТИКАЛЫҚ ТОТЫҒУ МЕН ТОТЫҚТЫРҒЫШ АММОНОЛИЗ РЕАКЦИЯЛАРЫНЫҢ МЕХАНИЗМІН ЗЕРТТЕУДЕГІ КВАНТТЫҚ ХИМИЯНЫҢ РӨЛІ

Тотықтырғыш аммонолиздің ванадий оксидті катализаторға реакциялық қабілеттілігі және метилпиридиндердің парциалды тотығудағы механизиін зерттеудегі кванттық химияның рөлі талқыланады. Химиялықғылымдар институтында жасалған жаңа тәсілді қолдану катализге тән құбылыстардың сипаты туралы гипотезаны алға жылжытуға, энергияның өтемақысы мен синергизм сияқты болжам жасауға мүмкіндік берді.

Түйін сөздер: кванттық химия, метилпиридиндер, реакциялық қаблеттілік, тотығу, тотықтырғыш аммонолиз, катализаторлар, механизм.

Резюме

П. Б. Воробьев, Т. П. Михайловская, А. М. Иманғазы

РОЛЬ КВАНТОВОЙ ХИМИИ В ИЗУЧЕНИИ МЕХАНИЗМА РЕАКЦИЙ КАТАЛИТИЧЕСКОГО ОКИСЛЕНИЯ И ОКИСЛИТЕЛЬНОГО АММОНОЛИЗА

Обсуждается роль квантовой химии в исследовании реакционной способности метилпиридинов и механизма их парциального окисления и окислительного аммонолиза на ванадийоксидных катализаторах. Применение разработанного в ИХН нового подхода позволило выдвинуть гипотезу о природе таких свойственных для катализа явлений, как промотирование, компенсация энергии и синергизм.

Ключевые слова: квантовая химия, метилпиридины, реакционная способность, окисление, окислительный аммонолиз, катализаторы, механизм.