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Oxidation of 3- and 4-Methylpyridines on Modified Vanadium Oxide Catalysts

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Abstract—The partial oxidation of 3- and 4-methylpyridines on V_2O_5 and vanadium oxide catalysts doped with TiO_2, Al_2O_3, and ZrO_2 was studied. The catalytic activities of the studied catalysts were correlated with the calculated proton affinities of the vanadyl oxygen. A possible mechanism of the surface stages of the partial oxidation of 3- and 4-methylpyridines on the vanadium oxide catalysts was discussed.

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Vanadium(V) oxide is the principal component of many alkylaromatic oxidation catalysts [1]. The activity and selectivity of V_2O_5 can be varied by doping it with other metal oxides, which increases the number of phases in the catalyst and forms different active centers. The multiphase nature of multicomponent V_2O_5 catalysts arises from the ability of V_2O_5 to form chemical compounds with modifying oxides under doping conditions [2]. The key role V_2O_5 plays in forming active and selective oxidation catalysts is explained by the fact that vanadium is a mixed-valence metal, as well as by the structure of this oxide, where the size of the V^{5+} cation allows both tetrahedral and octahedral configurations [3].

The aim of the present work was to study the partial oxidation of 3- and 4-methylpyridines on modified vanadium oxide catalysts and to correlate the catalytic activity of the catalysts with their chemical composition.

Our study of the partial oxidation of 3- and 4-methylpyridines on modified vanadium oxide catalysts revealed essential differences in the relative reactivities of the isomers and in the resulting aldehyde/acid ratios. 3-Methylpyridine, as a less reactive compound, shows a lower conversion, its major oxidation product is nicotinic acid, whereas pyridine-3-aldehyde is formed in small amounts, if any. 4-Methylpyridine is more reactive and, as a result, shows a higher conversion than 3-methylpyridine at the same temperature. Among the partial oxidation products of 4-methylpyridine we found, along with isonicotinic acid, pyridin-4-aldehyde, the yield of which in low-temperature experiments compares with the yield of the acid. This regularity is illustrated in Figs. 1 and 2 by the example of the catalyst with the V_2O_5:TiO_2 ratio of 1:8.

The predominant formation of nicotinic acid in the oxidation of 3-methylpyridine on the studied catalysts is likely to be associated with the activation of 3-methylpyridine on active centers of the oxide catalyst. The chemisorption of 3-methylpyridine probably involves interaction of the lone electron pair of the ring nitrogen atom with Brønsted acid centers (proton-donor centers) [4]. The 3-methyl group transforms into carboxyl without desorption of the intermediate pyridin-3-aldehyde into the gas phase. Such mechanism is favored by the steric structure of 3-methylpyridine. When the latter is in the chemisorbed state, the distance between its methyl group and the surface of the oxide catalyst allows interaction with nucleophilic oxygen. This interaction is also favored by the higher, compared to pyridin-4-aldehyde, proton affinity of the ring nitrogen in pyridin-3-aldehyde (Table 1), due to which the latter is stronger retained by the surface and only slightly desorbs to the gas phase. Evidence for the proposed mechanism was obtained in the experiments on high-temperature oxidation of 3-methylpyridine (350–370°C), when the contribution of substituent elimination is more essential. Under these conditions, by the ratio of the C_1 products (CO and CO_2) one can judge what direction of the

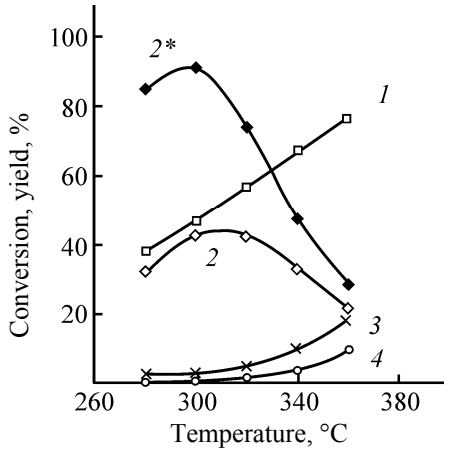


Fig. 1. Temperature effect on the oxidation of 3-methylpyridine on a 1:8 V_2O_5:TiO_2 catalyst. 3-Methylpyridine:O_2:H_2O molar ratio 1:22:118. (*1*) Conversion of 3-methylpyridine, (*2*) yield of nicotinic acid, (*2**) selectivity in nicotinic acid; yield of (*3*) pyridine and (*4*) CO_2.

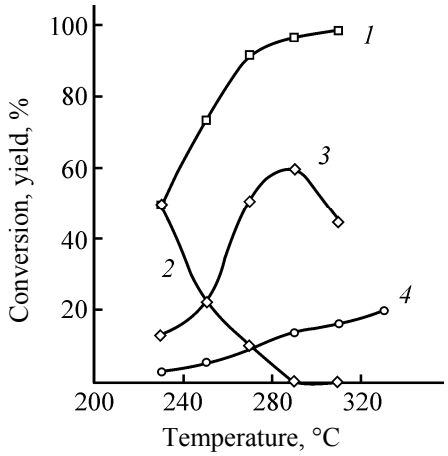


Fig. 2. Temperature effect on the oxidation of 4-methylpyridine on a 1:8 V_2O_5:TiO_2 catalyst. 4-Methylpyridine:O_2:H_2O molar ratio 1:14:110. (*1*) Conversion of 4-methylpyridine; yield of (*2*) pyridine-4-carboxaldehyde, (*3*) isonicotinic acid, and (*4*) CO_2.

transformation of the methyl group (aldehyde or acid) is prevailing. As shown previously, at temperatures characteristic of the oxidation of methylpyridines on vanadium oxide catalysts, CO is not oxidized into CO_2. In high-temperature experiments, among 3-methylpyridine oxidation products we found nicotinic acid, as well as its decarboxylation products pyridine and carbon dioxide; at the same time, carbon monoxide was absent, implying no aldehyde decarbonylation.

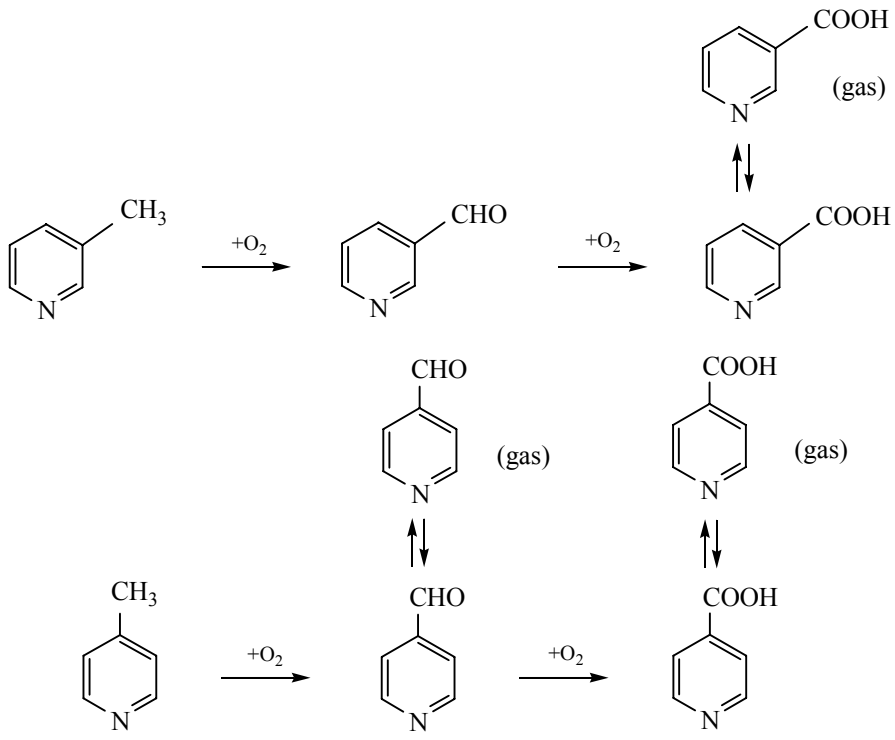
4-Methylpyridine is likely to be activated under catalysis conditions due to chemisorption on proton-donor centers of the catalyst surface, and the reaction center is shifted to the methyl group. In this case, quite an important role in the activation of the 4-methyl group belongs to its conjugation with the pyridine nitrogen. According to our semiempirical calculations (Table 1), the intermediate pyridin-4-aldehyde has a lower proton affinity (basicity) than pyridin-3-aldehyde and can be partially desorbed into the gas phase. By this reason, pyridin-4-aldehyde, along with isonicotinic acid, is always present in appreciable amounts among the products of the gas-phase catalytic oxidation of 4-methylpyridine.

As follows from data in Table 1, the electron-acceptor aldehyde substituent in the pyridine ring much decreases the proton affinity of the nitrogen heteroatom. It is readily seen that a more substantial decrease of basicity occurs, when the CHO substituent is introduced in position *4*. In terms of the classical organic chemistry, the different effects of the electron-acceptor substituent in positions *3* and *4* of the pyridine ring on the basicity of the nitrogen atom can be explained in the following way. The proton affinity of the pyridine nitrogen is the higher the less delocalized its lone electron pair. The electron-acceptor CHO group in position *4* is conjugated with the ring nitrogen atom and causes a stronger delocalization of its lone electron pair, thus causing a stronger basicity decrease. The CHO substituent in position *3* is not conjugated with nitrogen; as a result,

Table 1. Total energies (E_{tot}) and proton affinities (PA) of pyridine, pyridine-3-carboxaldehyde, and pyridine-4-carboxaldehyde and total energies of their nitrogen-protonated forms, calculated by the ab initio HF/6-31G* method

Compound	$-E_{tot}$, au		PA,[a] kJ mol^{-1}
	isolated molecules (M)	nitrogen-protonated forms (MH^+)	
Pyridine	246.5905850190	246.9739653228	1006.5
Pyridine-3-aldehyde	359.2646696951	359.6375903261	979.1
Pyridine-4-aldehyde	359.2632503286	359.6345137696	974.7

[a] $PA = (E_M - E_{MH^+})\cdot 627.5\cdot 4.184$.



it is less involved in delocalization of its lone electron pair and to a lesser extent decreases the basicity of the molecule.

Our research on the oxidation of 3- and 4-methylpyridines on vanadium oxide catalysts promoted by various oxide additives showed that an essential role in forming active and selective catalysts for these processes is played by chemical compounds between vanadium pentoxide and promoter oxides. Study of the chemical and phase composition of the 2:1, 1:1, and 1:2 V_2O_5:Al_2O_3 catalysts before and after 3-methylpyridine oxidation revealed no effect of the reaction medium on these catalyst characteristics. The all catalysts had the same components before and after experiments. The 2:1 V_2O_5:Al_2O_3 catalyst contained aluminum orthovanadate and minor amounts of V_2O_5 and V_3O_7, the 1:1 V_2O_5:Al_2O_3 catalyst was aluminum orthovanadate exclusively, and the 1:2 V_2O_5:Al_2O_3 catalyst contained aluminum orthovanadate, as well as γ-Al_2O_3, V_6O_{13}, and δ-Al_2O_3. It should be noted that aluminum orthovanadate was found to be stable under the 3-methylpyridine oxidation conditions. The interplanar spacings and $AlVO_4$ line intensities in the X-ray patterns of spent catalysts were the same as for freshly prepared samples. In the 2:1 V_2O_5:Al_2O_3 catalyst which contained free V_2O_5 along with aluminum orthovanadate, no V_2O_5 reduction was observed after the catalyst had been used in the oxidation reaction. This finding implies that the oxidation of 3-methylpyridine on oxide vanadium–aluminum catalysts occurred by an associative mechanism [5], involving oxygen adsorbed from the gas phase, rather than the catalyst lattice oxygen. Presumably, just the presence of a stable chemical compound ($AlVO_4$) in the catalysts was responsible for the fact that the oxidation of 3-methylpyridine occurred by an associative rather than a redox mechanism, and the active components of vanadium–aluminum oxide catalysts was aluminum orthovanadate. The resulting data are consistent with the results of 3-methylpyridine oxidation on V–Mo–O catalysts, which showed that 3-methylpyridine, unlike its 2- and 4-isomers, is oxidized exclusively by gaseous oxygen [4]. The oxidation of the 4-isomer involves lattice oxygen, and in the case of the 2-isomer, partial oxidation involves lattice oxygen, while complete oxidation involves both lattice and gaseous oxygen. The stability of the chemical and phase composition of vanadium–aluminum oxide catalysts in the reaction medium ensured stable operation of these catalysts.

The catalytic properties of an individual aluminum oxide used to promote vanadium pentoxide in the oxidation of 3-methylpyridine into nicotinic acid can

be evaluated by the results presented in Fig. 3. As seen, the conversion of the starting compound is low, which implies a low catalytic activity of aluminum oxide. The latter was found to differ from the other catalysts tested in 3-methylpyridine oxidation in that nicotinic acid was absent from the catalysate over the entire temperature range studied. The major reaction product with this catalyst was pyridine whose yield at 300°C was 84.5%. Thus, aluminum oxide proved to be an efficient catalyst of oxidative demethylation of 3-methylpyridine, which allows a highly selective formation of pyridine.

As seen from Fig. 3, at a 3-methylpyridine:O_2:H_2O molar ratio of 1:22:177, contact time 0.82 s, and temperature 300°C, vanadium pentoxide showed a low activity and selectivity. The conversion of 3-methylpyridine on this catalyst was as low as 18.5%, and the yields of the reaction products, specifically nicotinic acid (9%) and pyridine (5.5%), was very low. Promoting V_2O_5 with aluminum oxide additions much improved the efficiency of catalysis in 3-methylpyridine oxidation. Thus, a 21.9% addition of aluminum oxide in V_2O_5 raised the conversion of 3-methylpyridine and the yield of nicotinic acid by 30 and 38.5%, respectively. When the γ-Al_2O_3 addition in V_2O_5 was increased to 35.9%, the conversion of 3-methylpyridine and the yield of nicotinic acid further increased. The activity and selectivity of the vanadium–aluminum catalyst containing 52.9% of γ-Al_2O_3 are lower but still are higher compared to V_2O_5. Aluminum oxide less actively catalyzed 3-methylpyridine oxidation than mixed vanadium–aluminum catalysts but more actively than V_2O_5. The difference was that on vanadium pentoxide 3-methylpyridine converted into nicotinic acid and pyridine, whereas on Al_2O_3 it converted only into pyridine.

As seen from the resulting data, mixed vanadium–aluminum oxide contacts proved more efficient catalysts for oxidizing the starting pyridine bases into nicotinic acid than their constituents V_2O_5 and γ-Al_2O_3. Of the vanadium–aluminum catalysts the best one was found to be V_2O_5:Al_2O_3 = 1:1. This catalyst provided the highest yield (64%) and a highly selective formation of nicotinic acid (94.1%). With V_2O_5:Al_2O_3 = 2:1, the yield of the acid was no higher than 47%, but the selectivity of its formation reached 95.7%.

The results of X-ray phase analysis of the tested catalysts and their catalytic activity in 3-methylpyridine oxidation led us to a suggestion that the activity and selectivity of vanadium pentoxide promoted by varied amount of aluminum oxide vary depending on the chemical and phase composition of the catalysts. As the catalysts were sintered, Al_2O_3 and V_2O_5 reacted with each other to form a new phase (aluminum orthovanadate). The resulting samples differed from each other in that V_2O_5:Al_2O_3 = 2:1 contained excess V_2O_5, whereas V_2O_5:Al_2O_3 = 1:2 contained excess Al_2O_3. Equimolar amounts of Al_2O_3 and V_2O_5 (V_2O_5:Al_2O_3 = 1:1) completely reacted with each other to form a chemical compound ($AlVO_4$). According to our findings, the latter catalyst, specifically aluminum orthovanadate, exhibited the best catalytic properties in 3-methylpyridine oxidation. The catalysts containing V_2O_5 or γ-Al_2O_3 along with the chemical compound showed both lower activity and lower selectivity. Testing an individual γ-Al_2O_3 in 3-methylpyridine oxidation showed that this catalyst differs in its nature from the other tested samples and, therefore, exhibits quite a different catalytic action. Compared to V_2O_5 and vanadium–aluminum catalysts [6], γ-Al_2O_3 has a larger specific surface area and a

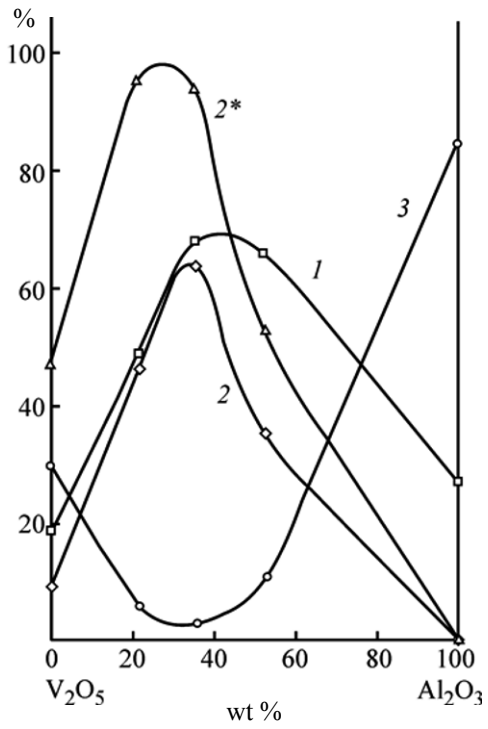


Fig. 3. Effect of the composition of the vanadium–aluminum oxide catalyst on the oxidative transformations of 3-methylpyridine. Rate of 3-methylpyridine feeding 15 g l^{-1} catalyst h^{-1}; 3-methylpyridine:O_2:H_2O molar ratio 1:22:177, contact time 0.82 s, 300°C. (*1*) Conversion of 3-methylpyridine, (*2*) yield of isonicotinic acid, and selectivity in (*2**) isonicotinic acid and (*3*) pyridine.

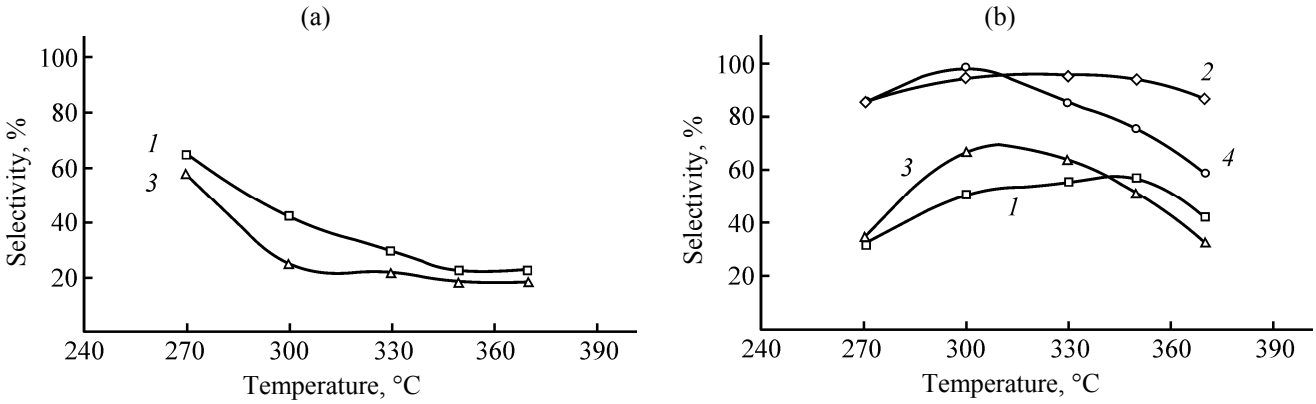


Fig. 4. Dependence of the selectivity of (a) pyridine-4-carboxaldehyde and (b) isonicotinic acid formation on temperature under the conditions of partial 4-methylpyridine oxidation on (*1*) V_2O_5, (*2*) $V_2O_5 \cdot 8TiO_2$, (*3*) $V_2O_5 \cdot Al_2O_3$, and (*4*) $V_2O_5 \cdot ZrO_2$. Rate of 4-methylpyridine feeding 35 g/l catalyst/h. 4-Methylpyridine:O_2:H_2O molar ratio 1:14:26.

higher surface activity. Due to such characteristics, aluminum oxide can serve as a potent decarboxylating and demethylating agent, thereby preventing accumulation of nicotinic acid and favoring formation of pyridine during 3-methylpyridine oxidation.

Thus, we showed that the catalytic properties of oxide catalysts in 3-methylpyridine oxidation vary with the nature and composition of the catalyst. Promoting V_2O_5 by aluminum oxide improves the catalytic action of the former oxide in 3-methylpyridine oxidation and allows nicotinic acid to be obtained in 94.1–95.7% selectivity. The promoting effect of Al_2O_3 on V_2O_5 is explained by that the promoter changes the chemical and phase composition of the catalyst. The Al_2O_3 promoter reacts with vanadium pentoxide to form aluminum vanadate which is the principal active component of vanadium–aluminum catalysts. At an equimolar ratio of the initial components in a vanadium–aluminum oxide catalyst, the promoter completely reacts with vanadium pentoxide to form a chemical compound, and this ensures formation of a mechanically strong and steadily functioning catalyst showing a fairly high efficiency in the oxidation of 3-methylpyridine into nicotinic acid.

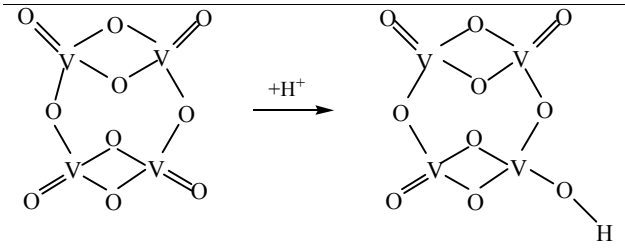
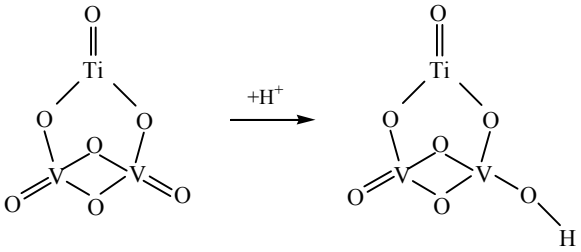
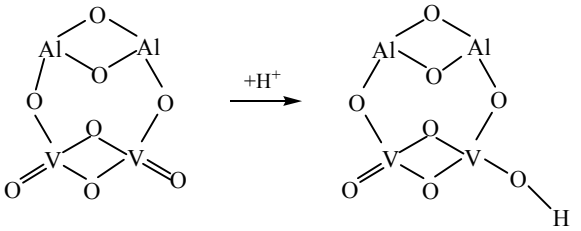
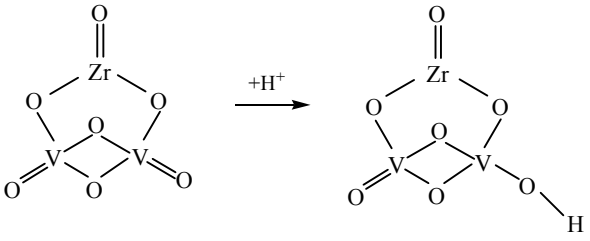
In view of the above-described results, we considered it of interest to find out how the selectivity of the partial oxidation of 4-methylpyridine on vanadium oxide catalysts depends on the nature of the promoter oxide.

Figure 4 presents the results of 4-methylpyridine oxidations in comparable conditions on an individual vanadium pentoxide and on binary vanadium oxide catalysts modified by titanium, aluminum, and zirconium oxide additions. As seen from Fig. 4, binary catalysts provide a more selective formation of isonicotinic acid than V_2O_5. The nature of the promoter oxide appreciably affects the selectivity of binary catalysts in 4-methylpyridine oxidation under the studied conditions. The sole product of the partial oxidation on V–Ti and V–Zr oxide catalysts is isonicotinic acid. The selectivity of its formation in low-temperature experiments is 85–98%. In the oxidation of 4-methylpyridine on an individual V_2O_5 and on a binary V–Al oxide catalyst, we found, along with isonicotinic acid, pyridine-4-carboxaldehyde in appreciable amounts.

According to published data [1, 7–10], in the conditions of vapor-phase catalytic oxidation of methylaromatic compounds, the hydrogen abstracted from oxidized methyl groups can be accepted by various oxygen species bound with vanadium, including the double-bonded V=O lattice oxygen. It was interesting to compare the catalytic properties of an individual vanadium pentoxide and the studied binary oxide catalysts modified by TiO_2, Al_2O_3, and ZrO_2 with the calculated proton affinities of the vanadyl oxygen in these catalysts.

The selectivity of formation of isonicotinic acid on all the modified catalysts is higher than on V_2O_5. The nucleophilicity of the vanadyl oxygen in the binary catalysts, calculates as proton affinity by the extended Hückel method supplemented by the Andersen repulsive potential, in the cluster approximation (Table 2). The active centers of catalysts were modeled by clusters containing V_2O_5 and promoter oxide fragments. The calculation results gave us grounds to

Table 2. Total energies (E_{tot}) of vanadium-containing clusters and their protonated forms and proton affinities (PA) of the vanadyl oxygen, calculated by the extended Hückel method supplemented by the Andersen repulsive potential

Reaction	$-E_{tot}$, eV/mol		PA,[a] kJ mol^{-1}
	initial state	final state	
	1578.056478	1580.544012	240.1
	1103.490764	1106.016159	243.8
	1257.130681	1259.652720	243.4
	1105.525449	1108.062561	244.9

[a] PA = $(E_{init} - E_{fin})\cdot 23.07\cdot 4.184$.

conclude that the observed effects of the additives on the selectivity of the binary catalysts are explained by the fact that the additives affect the nucleophilicity of the vanadyl oxygen which is involved in deprotonation of the methyl substituent to be oxidized.

Thus, our study of the partial oxidation of 3- and 4-methylpyridines on V_2O_5 and vanadium oxide catalysts modified by TiO_2, Al_2O_3, and ZrO_2 additions established that the increase of the catalytic activity of vanadium pentoxide by promoter oxides may be associated with an enhancement of the nucleophilicity (proton affinity) of the vanadyl oxygen. It was suggested that the different relative yields of pyridinecarboxaldehydes and pyridinecarboxylic acids in the partial oxidation of 3- and 4-methylpyridines on vanadium oxide catalysts is explained by differences in the basicities and adsorbtivities of the intermediate pyridine carboxaldehydes.

EXPERIMENTAL

3- and 4-Methylpyridines of pure grade were dried and distilled. Their physicochemical characteristics

were consistent with those reported for individual compounds: 3-methylpyridine, bp 140°C (692 mm Hg), d_4^{20} 0.9566, n_D^{20} 1.5050; 4-methylpyridine, bp 141°C (695 mm Hg), d_4^{20} 0.9548, n_D^{20} 1.5058 [11].

Catalysts with varied contents of V_2O_5 and promoter oxides were prepared by calcination of oxides of analytical grade. X-ray phase analysis was performed on a DRON-7 instrument (CoK_α radiation).

Vapor-phase oxidation of 3- and 4-methylpyridines was performed on a laboratory flow-through device; its design is described in [12]. Reaction products were trapped in airlift wet scrubbers. Conditions of chromatographic analysis of 3-methylpyridine, 4-methylpyridine, and pyridine-4-carboxaldehyde are described in [13]. Nicotinic and isonicotinic acids were titrated with alkali. Profound oxidation products were analyzed on an LKhM-8MD gas chromatograph with a thermal conductivity detector. Stainless-steel columns 3.5 m in length and 3 mm in internal diameter, packed with an AG-5 charcoal (0.25–0.50 mm) for CO analysis and Polysorb-1 (0.16–0.20 mm) for CO_2 analysis. The oven temperature was 40°C. The analyte balance was 95–100% in all experiments.

Quantum-chemical calculations of unsubstituted pyridine and pyridine-3- and pyridine-4-carboxaldehydes were performed using WinGAMESS [14]. The clusters modeling the active surface centers of modified catalysts were calculated in the cluster approximation [15] by the extended Hückel method, using the program developed at the Laboratory of Quantum Chemistry, Boreskov Institute of Catalysis, Siberin Branch, Russian Academy of sciences (Novosibirsk). The calculation procedure was described in [16].

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