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Mechanism of the oxygen involvement in nicotinic acid formation under β-picoline oxidation on V-Ti-O catalyst

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ABSTRACT

Mechanism of the oxygen involvement in nicotinic acid formation under β-picoline oxidation on vanadia-titania catalyst was studied by *in situ* FTIR spectroscopy and kinetic method in temperature range of 120–300 °C. The formation of nicotinic acid proceeds via a consecutive transformation of the surface carbonil-like and carboxylate complexes stabilized at reduced vanadium. Catalyst oxygen includes in formation of these complexes. Carboxylate is a direct precursor of nicotinic acid, it turns into nicotinic acid in the presence of the gas-phase oxygen in joint step of catalyst reoxidation–acid desorption. Significant concentration ratio of oxygen to β-picoline ($C_{O2}:C_{\beta P} > 16:1$) is necessary to effective running reaction. This factor can be explained by the reaction mechanism. The variety of oxygen functions and of oxygen species require the maximum oxidized state of the catalyst and explain the necessity of a high oxygen excess in the reaction mixture.

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1. Introduction

Nicotinic acid is a valuable chemical product and an important vitamin of B group. It is widely used in medicine, in food industry, in agriculture, and in production of cosmetics. Annual worldwide output of nicotinic acid is ~35,000 ton [1].

Nicotinic acid is produced commercially by oxidation of β-picoline in liquid phase mainly. Processes of liquid-phase oxidation by potassium permanganate, or nitric acid, or sulfuric acid are performed at high pressure. Nicotinic acid is also formed via hydrolysis of pyridine-3-nitrile that is produced by ammoxidation of β-picoline in the presence of vanadia-titania catalyst [1–3]. Both that methods have substantial drawbacks.

Boreskov Institute of Catalysis developed a direct one-step method of nicotinic acid synthesis by gas-phase oxidation of β-picoline by air over vanadia-titania catalyst [4]. The process produces no liquid wastes and no harmful gas exhausts, and the target product can be easily isolated. In total, the process meets all requirements of "green" technology. Nicotinic acid is the main product of the reaction. The selectivity to nicotinic acid exceeds 80% at about 95% of β-picoline conversion.

Formation of nicotinic acid over V_2O_5-TiO_2 catalyst directly from β-picoline and via intermediate product pyridine-3-carbaldehyde follows by a parallel-consecutive reaction scheme [5].

Many details of mechanism of nicotinic acid formation are still unclear. We have used infrared spectroscopy in our study as one of the most informative methods for studying mechanism of heterogeneous catalytic reactions.

Traditionally it is considered that the formation of a product in catalytic oxidation of hydrocarbons proceeds by Mars van Krevelen mechanism that includes separate steps of catalyst reduction with hydrocarbon substrate and subsequently its reoxidation by dioxygen. Here we would like to present the function of the oxygen in more detail. Two oxygen forms participate in products formation: catalyst oxygen includes in the formation of intermediates with simultaneous catalyst reduction and gaseous oxygen includes in conjugated step of catalyst reoxidation–product desorption.

2. Experimental

2.1. Catalyst preparation

The 20% V_2O_5-80% TiO_2 (wt.%) catalyst was prepared by spray drying of an aqueous suspension of vanadyl oxalate and TiO_2 (anatase, the BET 300 m^2/g) followed by its shaping and calcining in air at 450 °C [6]. The catalyst BET surface area was 25 m^2/g. According to the XRD data, the catalyst contained phases V_2O_5 and TiO_2 (anatase). The high activity vanadia-titania catalyst is due to the formation of V–O–Ti bonds on the coherent interface between V_2O_5 and TiO_2 particles [6]. This results in a change in the coordination environment of vanadium cations [6] and in the variation of the bond strength of lattice oxygen as compared to bulk vanadium oxide [7]. $H_3PW_{12}O_{40}\cdot 13H_2O$ heteropolyacid ($S = 5$ m^2/g) of chem-

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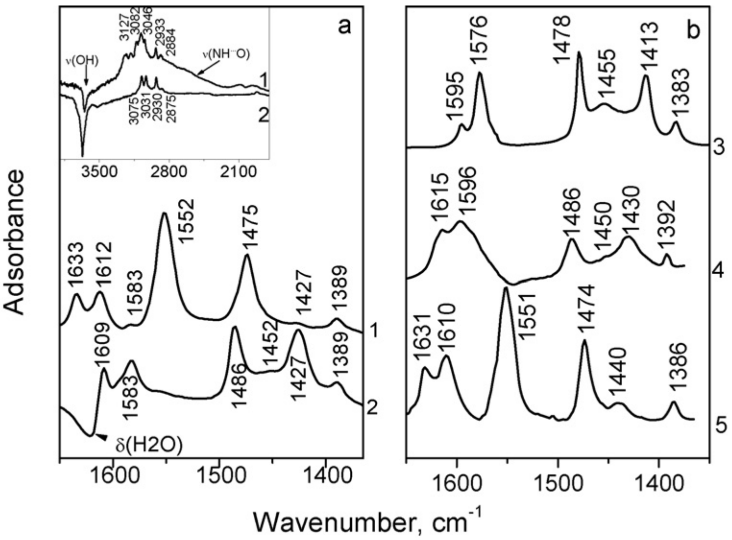

Fig. 1. FTIR spectra of β-picoline adsorbed on: (a) V_2O_5-TiO_2 (1) and TiO_2 (2); (b) pure β-picoline (3) and adsorbed on γ-Al_2O_3 (4), $H_3PW_{12}O_{40}$ (5) (the background spectra have been subtracted).

ical purity grade (twice recrystallized from water) and γ-Al_2O_3 (S = 250 m^2/g) were also used in this work.

2.2. Kinetic studies

The kinetic studies were carried in a differential reactor in a flow-circulating setup with chromatographic analysis of the reaction mixture components. The oxygen effect was studied at 270 °C at a constant conversion of β-picoline equal to 60 ± 2%. The conversion constancy was attained by variation of the contact time.

2.3. FTIR experiments

In situ FTIR spectroscopy experiments were performed in a flow IR cell-reactor with a Bomem MB-102 FTIR spectrometer. Catalyst powder (35–50 mg) was pressed into a self-supported 1 cm × 3 cm wafer. The wafer was mounted into a quartz IR cell-reactor with a CaF_2 windows and activated in air flow (50 cm^3/min) at 300 °C for 60 min. β-Picoline used for the adsorption was $C_5H_4NCH_3$ from Aldrich Chemical Company, Inc. (purity 99%). Pyridine-3-carbaldehyde used for the adsorption was C_5H_4NCHO from Aldrich Chemical Company, Inc. (purity 99%) Adsorption was carried out at 120 °C by injecting β-picoline or pyridine-3-carbaldehyde (1–2 μl) into air or helium flowing through the reactor cell. Next, the temperature was increased at a rate of 5 °C/min with additional IR spectra taken every 10 °C. The background IR spectra of samples were obtained at each temperature for their further subtraction.

3. Results and discussions

3.1. FTIR studies of β-picoline adsorption

Fig. 1a presents in situ FTIR spectra of adsorbed species formed on the V_2O_5-TiO_2 catalyst and TiO_2 during the β-picoline adsorption at 120 °C. Upon adsorption on TiO_2, the FTIR spectra show the bands at 3075, 3031 (ν(CH)ring), 2930, 2875 ($\nu(CH_3)$), 1609, 1583, 1486 (ν(CC, CN)ring), 1452 ($\delta_{as}(CH_3)$), 1427 (ν(CC, CN)ring) and 1389 ($\delta_s(CH_3)$) cm^{-1}. Upon the adsorption on V_2O_5-TiO_2 catalyst, the FTIR spectra show the bands at 3127, 3082, 3046 (ν(CH)ring), 2933, 2884 ($\nu(CH_3)$), 1633, 1612, 1583, 1552, 1475, 1427 (ν(CC, CN)ring) and 1389 ($\delta_s(CH_3)$) cm^{-1}, as well as a broad absorption band with a complicated contour in the frequency range of 3200–1800 cm^{-1}. β-Picoline adsorption both on V_2O_5-TiO_2 catalyst and on support led to decrease of intensity of the band due to stretching mode of hydroxyl group at ~3660 cm^{-1} (Fig. 1a). In the case of V_2O_5-TiO_2 catalyst the decrease of the intensity of this band was accompanied by simultaneous appearance of broad absorption in the range of 3200–1800 cm^{-1}. This fact is indicated on hydrogen bond formation. On the other hand, we did not observed any spectral manifestation of hydrogen bond formation during β-picoline adsorption on the support. Thus, β-picoline interacts with Lewis acid cites of the support. It is accompanied by the removal of hydroxyl group from the surface (Fig. 1a, negative band at 3660 cm^{-1}) and desorption of water (Fig. 1a, negative band at 1620 cm^{-1}). The comparison of the spectrum of β-picoline adsorbed on the V_2O_5-TiO_2 catalyst (Fig. 1) and spectra of β-picoline adsorbed on model samples ($H_3PW_{12}O_{40}\cdot 13H_2O$ heteropolyacid—strong Brönsted acid sites; γ-Al_2O_3—Lewis acid sites) (Fig. 1b) led us to conclude that β-picoline interacts both with strong Brönsted and with Lewis acid sites of V_2O_5-TiO_2 catalyst. Indeed, FTIR spectrum of β-picoline adsorbed on V_2O_5-TiO_2 catalyst is similar to spectrum of β-picoline adsorbed on $H_3PW_{12}O_{40}\cdot 13H_2O$ at 120 °C (Fig. 1a, spectrum 1 and Fig. 1b, spectrum 5). The presence of two additional weak bands at 1583 and 1427 cm^{-1} in the spectrum of β-picoline adsorbed on the V_2O_5-TiO_2 catalyst indicates that β-picoline interacts also with Lewis acid cites (see spectrum of β-picoline adsorbed on γ-Al_2O_3 at 200 °C: Fig. 1b spectrum 4). Previously, it was shown that β-picoline coordinates to strong Brönsted and Lewis acid sites of $CrV_{0.95}P_{0.05}O_4$ catalyst. The interaction with Brönsted acid sites results in activation of adsorbed β-picoline by withdrawing the electrons of pyridine ring [8].

3.2. FTIR studies of β-picoline and pyridine-3-carbaldehyde transformation

We have studied the transformation of β-picoline on V_2O_5-TiO_2 catalyst in the temperature range of 120–250 °C both in the presence and in the absence of O_2 in gas phase. The increase of reaction temperature led to gradual decrease of intensity of the bands due to methyl group vibrations (Fig. 2a). At 150 °C both in the presence and in the absence of oxygen in gas flow we observed the appearance of new band at 1670 cm^{-1} due to carbonyl stretching

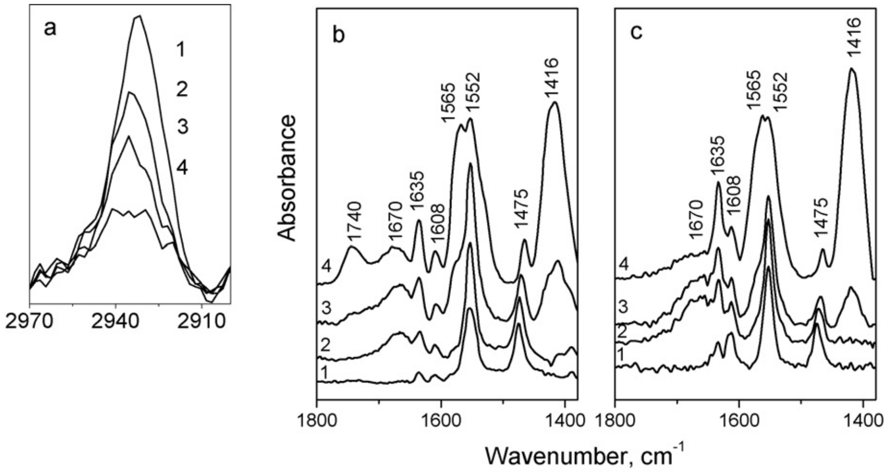

Fig. 2. FTIR spectra β-picoline adsorbed on V_2O_5-TiO_2 at different temperatures in the air flow (a and b) and in the He flow (c): (1) 120 °C, (2) 150 °C, (3) 200 °C, (4) 250 °C (the background spectra have been subtracted).

mode (Fig. 2b and c). The similar band we also observed in spectra measured during adsorption of pyridine-3-carbaldehyde on the same catalyst [9]. Thus, it seems reasonable to assign this band to C=O stretching mode of aldehyde surface complex formed under β-picoline oxidation. Oxygen of the catalyst participates in the formation of this complex. Since the concentration of this complex is essentially higher in oxygen-free atmosphere, it is very likely that oxygen of gas phase results in decomposition of aldehyde complex with pyridine-3-carbaldehyde release into gas phase.

At 200 °C both in the presence and in the absence of O_2 in gas flow we observed the appearance of two new bands at 1565 and 1416 cm^{-1} due to stretching modes of carboxylate surface complexes (Fig. 2). We associate the appearance of these bands with formation of surface salt of nicotinic acid (nicotinate) [10]. The increase of the temperature to 250 °C led to considerable raise of the intensity of the bands at 1565 and 1416 cm^{-1} (Fig. 2) both in the presence and in the absence of O_2 in gas flow, but in the presence of gas phase O_2 the intensity of nicotinate bands was noticeably lower. In addition, only in the presence of the oxygen in gas flow at 200–250 °C we observed in the spectra band at 1740 cm^{-1} due to carboxyl stretching mode of molecular adsorbed nicotinic acid (Fig. 2). Thus, surface nicotinate is direct precursor of nicotinic acid. The oxygen of catalyst participates in nicotinate formation. Gas phase O_2 assist in transformation of nicotinate into nicotinic acid.

Fig. 3 represents in situ FTIR spectra of adsorbed species on the V_2O_5-TiO_2 catalyst after the β-picoline adsorption at the temperature 300 °C and at consequent decreasing the temperature in the flow of air (Fig. 3a) and He (Fig. 3b). Both in the presence and in the absence of oxygen in gas phase only surface nicotinate (spectra 1, Fig. 3a and b) is formed during β-picoline adsorption at 300 °C (bands at 1565 and 1416 cm^{-1}). The band at 1740 cm^{-1} of molecular adsorbed nicotinic acid appears in spectra at 200 °C (spectrum 2, Fig. 3a) into air flow. Intensity of the band at 1740 cm^{-1} increases under decreasing temperature indicating on the readsorption of

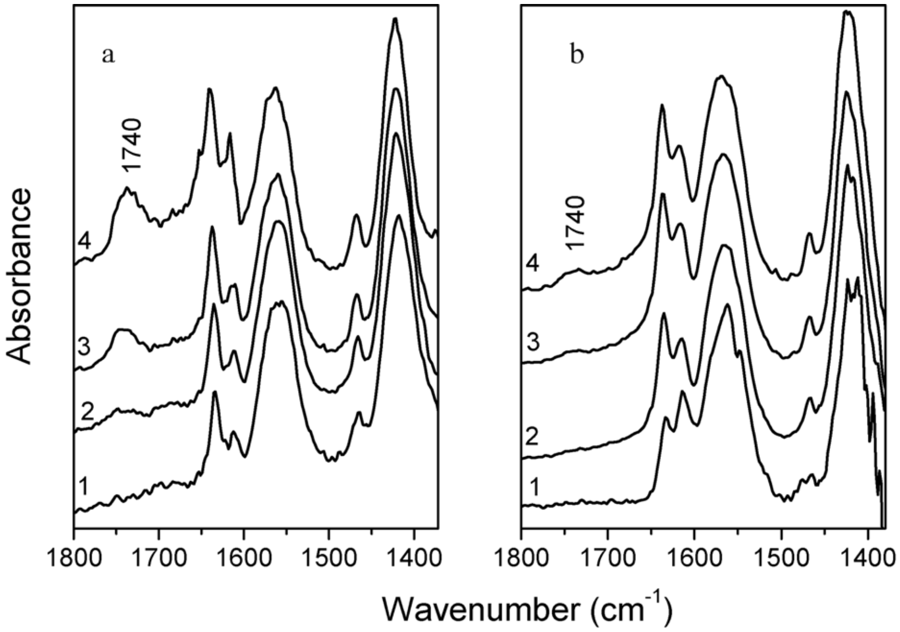

Fig. 3. FTIR spectra of adsorbed species on the V_2O_5-TiO_2 catalyst after the β-picoline adsorption at 300 °C (1) and at consequent decreasing temperature down to 200 °C (2), 100 °C (3) and 50 °C (4) in the flow of air (a) and He (b).

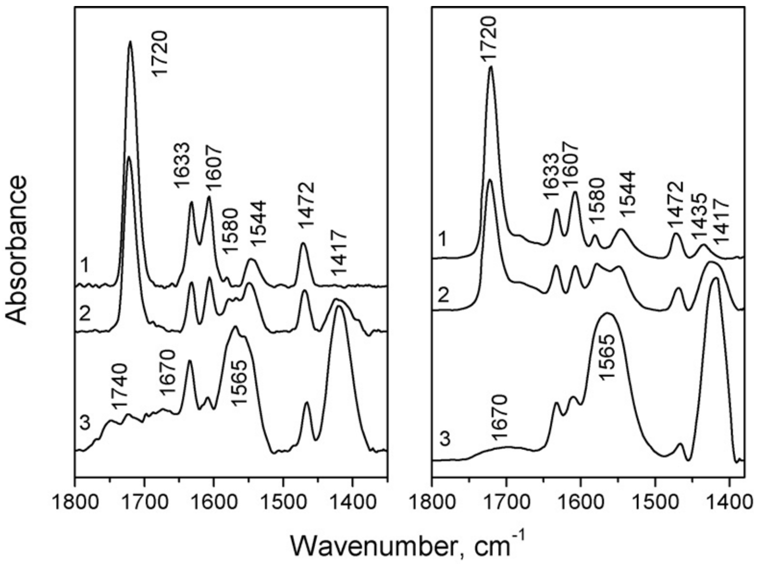

Fig. 4. FTIR spectra pyridine-3-carbaldehyde adsorbed on V_2O_5-TiO_2 at different temperatures in the air flow (a) and in the He flow (b): (1) 120 °C, (2) 200 °C, (3) 250 °C (the background spectra have been subtracted).

nicotinic acid from gas phase. In helium flow very weak band at 1740 cm^{-1} appears only at 50 °C (spectrum 4, Fig. 3b) indicating on minor content of nicotinic acid in gas phase. These data support the participation of gas phase O_2 in nicotinate decomposition and simultaneous nicotinic acid desorption.

Infrared spectra obtained during pyridine-3-carbaldehyde adsorption on V_2O_5-TiO_2 catalyst at high temperatures were very similar to spectra collected at the same temperatures during β-picoline oxidation (see Figs. 2 and 4). The transformation of pyridine-3-carbaldehyde into nicotinic acid also occurs through formation of intermediate surface nicotinate [9]. The presence of the dioxygen in gas phase is required for further transformation of nicotinate into nicotinic acid (Fig. 4a, spectrum 3). Indeed, only in the presence of gas phase O_2 we observed the appearance of the band at 1740 cm^{-1} of adsorbed nicotinic acid (Fig. 4).

3.3. *The scheme of nicotinic acid formation and the effect of the oxygen*

Fig. 5 represents the scheme of the mechanism of nicotinic acid formation [11]. The nicotinic acid formation proceeds at two routes: via direct β-picoline oxidation and via intermediate pyridine-3-carbaldehyde oxidation. Nicotinic acid forms through a sequence of similar surface complexes both at oxidation of β-picoline (steps 2, 4 and 5) and at oxidation pyridine-3-carbaldehyde (steps 6, 6′ and 7). Pyridine-3-carbaldehyde formation runs at 2, 3 steps. Adsorption of both β-picoline and pyridine-3-carbaldehyde is accompanied by active center reduction. Selective oxidation proceeds over hydrated active sites. The water addition strongly increase the rate of nicotinic acid formation on V_2O_5-TiO_2 catalyst [5] due to generation of Brönsted acid cites [8].

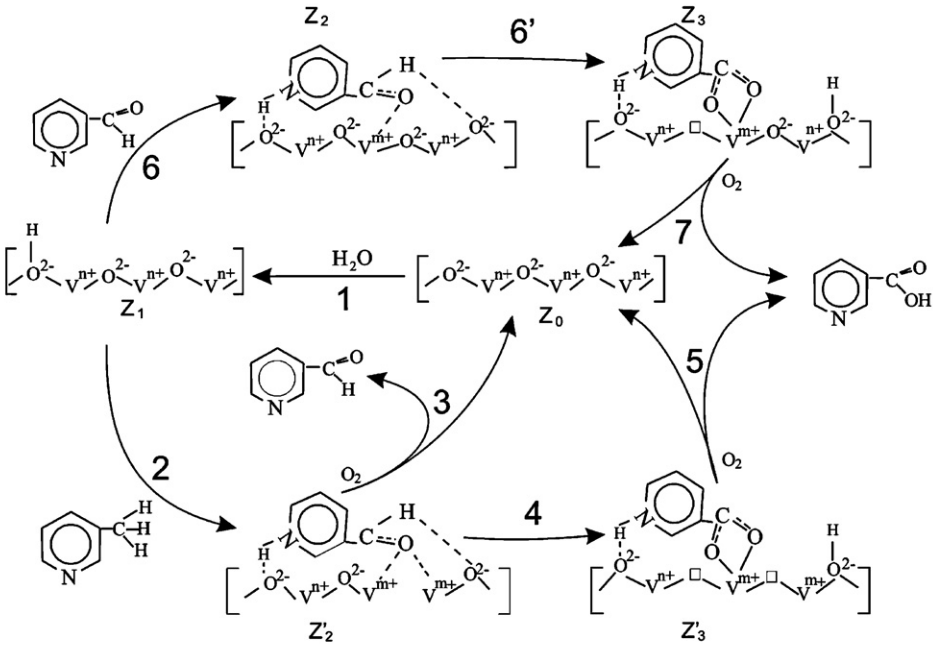

Fig. 5. The scheme of the mechanism of nicotinic acid formation (Z_0 is an oxidized site, Z_1 is a hydrated site, Z_2 and Z'_2 are carbonyl complexes Z_3 and Z'_3 are carboxylate complexes, n^+ is 5^+ and m^+ is 4^+ or 3^+).

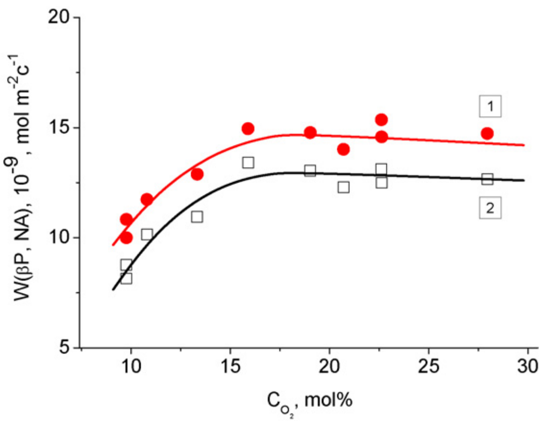

Fig. 6. The dependence of the rate of β-picoline consumption (1) and nicotinic acid formation (2) upon oxygen concentration. $X = 60 \pm 1\%$; $t = 270\,^{\circ}C$; β-picoline:O_2:H_2O = 1:(9–23):20 mol%, balance N_2. The points are experimental data; lines are calculated according to kinetic equations.

Based on the proposed mechanism of the reaction kinetic model was elaborated and kinetic rate equations were derived by using graph theory. The description of kinetic model, procedure of kinetic equations derivation in detail and calculated kinetic constants are given in [11].

Fig. 6 shows the dependencies of rates of β-picoline consumption and nicotinic acid accumulation on the steady-state concentration of oxygen. β-Picoline conversion as well as concentrations of β-picoline, water vapor and nicotinic acid were kept constant. The oxygen concentration in the inlet reaction mixture was changed from 9 to 23 mol%. The rate of β-picoline consumption and the rate of nicotinic acid formation reveal a tendency to saturation as oxygen concentration increases. The curves are coming to a plateau at above 16 mol%. The points are experimental data; lines are calculated according to kinetic equations based on proposed mechanism considered the participation of two oxygen forms in nicotinic acid formation. As one can see calculated curves fit experimental points very well. A high concentration ratio of oxygen to oxidizable reagent is typical in the selective oxidation of heterocyclic compounds [12–14], including β-picoline [15,16].

Effect of gas phase oxygen consists in decreasing the bond strength of nicotinate with active center. The similar mechanism of carboxyl acid formation over the same V_2O_5-TiO_2 catalyst was shown for reaction of formaldehyde oxidation [17]. During interaction of formaldehyde and lattice oxygen carboxylate (formate) coordinated to reduced vanadium active center is formed. Formate is the direct precursor of formic acid. Formic acid desorbs into the gas phase in the presence of O_2 only. According to DFT calculations [18] the heat of desorption of the acid from reduced vanadium cite is about 33 kcal mol^{-1}. The heat of formic acid desorption from oxidized cite is equal to 16 kcal mol^{-1}. These values characterize the bond strength of surface carboxylates. Strongly bound surface formate is dead end complex and transforms into formic acid only in the stage joined with catalyst reoxidation.

The decrease of bond strength of surface carboxylates with oxidized active center leads to decomposition of surface complex without destruction of carbon skeleton and directs the reaction to selective oxidation channel.

The similar mechanism of the β-picoline oxidation was demonstrated for $VCr_{0.95}P_{0.05}O_4$ catalyst [8]. The nicotinic acid formation proceeds via a consecutive transformation of the same surface complexes—aldehyde-like and carboxylate stabilized at reduced vanadium. The difference of proposed reaction mechanism for VCrPO and V_2O_5-TiO_2 catalysts consist in interpretation of gaseous oxygen function. According to Takehira et al. [8], the effect of the oxygen consist in filling the oxygen vacancies and further it participation in surface complex formation (see Scheme 3 [8]). The formation of oxygenated products in the absence of gaseous oxygen [8] supports this idea. In the case of V_2O_5-TiO_2 catalysts gaseous oxygen reoxidates the reduced active cites with coordinated surface complexes and thus promotes decomposition of the intermediates with evolving target products.

4. Conclusion

The β-picoline oxidation to nicotinic acid over V_2O_5-TiO_2 follows by a parallel-consecutive reaction scheme directly from β-picoline and via intermediate product pyridine-3-carbaldehyde.

The formation of nicotinic acid from both β-picoline and pyridine-3-carbaldehyde proceeds via a consecutive transformation of the same surface complexes—aldehyde-like and carboxylate stabilized at reduced vanadium. These complexes include the catalyst oxygen.

Carboxylate complex is a direct precursor of nicotinic acid. It turns into acid only in the presence of the gas-phase oxygen. Two oxygen forms participate in nicotinic acid formation: catalyst oxygen includes in formation of nicotinate and gaseous oxygen includes in conjugated step of catalyst reoxidation–acid desorption. Effect of gas phase oxygen consists in decreasing the bond strength of nicotinate with reduced active center during catalyst reoxidation.

A complicated mechanism and the variety of oxygen functions and of oxygen species require the maximum oxidized state of the catalyst and explain the necessity of a high oxygen excess in the reaction mixture.

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