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Mechanism of Carboxylic Acid Formation on Vanadium-Containing Oxide Catalysts

G. Ya. Popova, T. V. Andrushkevich, I. I. Zakharov, and Yu. A. Chesalov

Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

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Abstract—The surface intermediates in acrolein oxidation into acrylic acid on a V–Mo oxide catalyst, formaldehyde oxidation into formic acid on a V–Ti catalyst, and 3-pyridinecarboxaldehyde and β-picoline oxidation into nicotinic acid on a V–Ti catalyst are identified by *in situ* IR spectroscopy. The acids are found to form by similar mechanisms. The intermediates in acid formation are saltlike surface compounds (formates, acrylates, and nicotinates) stabilized on vanadium ions. The role of vanadium in acid formation is discussed in terms of the mechanisms suggested.

Carboxylic (formic, acetic, acrylic, methacrylic, benzoic, nicotinic, etc.) acids are valuable chemicals widely used in the production of polymers, artificial fibers, odorants, and a variety of other organic compounds. The synthesis of acrylic acid by acrolein oxidation on a V–Mo oxide catalyst and the synthesis of methacrylic acid by methacrolein oxidation catalyzed by salts of a P–Mo–V heteropoly acid have been commercialized. Active and selective catalysts have been developed for the synthesis of other carboxylic acids. For example, the V_2O_5/TiO_2 catalyst is highly selective in the production of formic acid by direct oxidation of formaldehyde [1], in butene oxidation into acetic acid [2], in β-picoline oxidation into nicotinic acid [3], and in toluene oxidation into benzoic acid [4]. The V_2O_5 and V_2O_5/SnO_2 catalysts are active and selective in the oxidation of benzaldehyde and *o*-tolualdehyde into benzoic acid [5, 6]. In the last few years, there has been great interest in the production of acrylic and acetic acids by direct oxidation of propane and ethane, respectively. The highest yield of acrylic acid was achieved with MoVTeNbO catalysts [7]; the highest yield of acetic acid, with MoVNbO catalysts [8].

As is clear from the above, vanadium is a necessary component of catalysts for carboxylic acid synthesis.

Here, based on the results of mechanistic studies, we report the role of vanadium in the oxidation of formaldehyde, acrolein, and β-picoline into formic, acrylic, and nicotinic acids, respectively, on vanadium- containing oxide catalysts.

EXPERIMENTAL

Vanadium–titanium oxide (V–Ti) catalysts were prepared by spraying a titanium dioxide (anatase) suspension in an aqueous solution of vanadium oxalate [1, 3], and vanadium–molybdenum oxide (V–Mo) catalysts were prepared by spraying an aerosol suspension in an aqueous solution of ammonium paramolybdate and ammonium metavanadate followed by drying at 110°C [9]. The V–Ti catalysts were calcined in air at 400 or 450°C for 4 h. The V–Mo catalysts were calcined in air at 300°C for 4 h and in an acrolein-containing mixture at 430°C for another 4 h.

Catalytic tests were carried out in a circulation reactor at atmospheric pressure, the reaction mixture being analyzed chromatographically.

In situ IR spectroscopic studies were carried out in a 1.5-cm^3 high-temperature flow-through reactor cell similar to the cell described in [10]. A catalyst pellet of dimensions 1×3 cm and weight ~50 mg was placed in the cell and was aged there in flowing air at a prescribed temperature. Next, the cell was cooled to a prescribed adsorption temperature, the air flow was replaced with a reaction mixture flow, and IR spectra were recorded at certain intervals. The decomposition of surface intermediates was studied both in the presence and in the absence of oxygen in the reaction mixture.

Quantum chemical analysis of the electronic mechanism of the reaction and modeling of the AS were carried out by SCF MO–LCAO *ab initio* calculations. The geometry of surface molecular systems was completely optimized using a double-ξ basis set of 3-21G* Gaussian functions. For vanadium atoms, we used a Gaussian basis set simulating the double-ξ basis set described in [11]. All calculations were made using the Gaussian 92 program [12].

RESULTS AND DISCUSSION

Catalytic Properties

Our studies of a wide variety of multicomponent oxide catalysts have demonstrated that the V–Ti system is the most active in the oxidation of formaldehyde into formic acid and of β-picoline into nicotinic acid [1, 3]

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Table 1. Selective oxidation into acids on V–Mo–O catalysts

No.	Reaction	V_2O_5/MeO_n	T, °C	Feed composition, vol %	S, %	Acid yield, %
1	$CH_2O \longrightarrow CH_2O_2$	20% V_2O_5 80% TiO_2	120	CH_2O 6.5, H_2O 8, air	90	85
2	$C_5H_4NCH_3 \longrightarrow C_5H_4NCHO_2$	20% V_2O_5 80% TiO_2	300	C_6H_7N 1, H_2O 20, air	86	83
3	$C_3H_4O \longrightarrow C_3H_4O_2$	12.5% V_2O_5 87.5% MoO_3	260	C_3H_4O 4, H_2O 20, air	98	94

and the V–Mo system is the most active in acrolein oxidation into acrylic acid [9].

By testing V–Mo [9] and V–Ti [1, 3] oxide systems in a wide range of V : Me ratios, we optimized the catalyst composition for each of the reactions. Data characterizing the performance of the optimized catalysts are listed in Table 1 [9, 13].

Mechanism of Carboxylic Acid Formation

Our mechanistic study included identification of the intermediate surface compounds (SCs) of the substance oxidized and the reaction products, ascertainment of the role of these SCs in the formation of the reaction products, and elucidation of the way oxygen is involved in the formation of the reaction products.

Mechanism of formaldehyde oxidation on the V–Ti catalysts. Earlier, we found by *in situ* IR spectroscopy at 100–200°C [14] that the surface intermediates resulting from the interaction between formaldehyde and the V–Ti catalyst that had been calcined at 450°C (VTi450) are two-phase systems consisting of V_2O_5 and vanadium-doped TiO_2 (anatase) [15]. The structures of the identified surface complexes and the temperature ranges in which these complexes were observed are presented in Table 2.

Here, we report the surface intermediates forming during the selective oxidation of formaldehyde on the V–Ti catalyst that has been calcined at 400°C (VTi400). Lowering the calcination temperature from 450 to 400°C increases the specific surface area from 30 to 140 m^2/g and changes the state of the surface. The surface of the VTi400 catalyst is nearly a vanadyl monolayer, containing eight or nine V atoms per square nanometer, and is free of V_2O_5 crystals. The difference in phase composition between VTi400 and VTi450 shows itself in the IR spectra of the catalysts themselves and the adsorbed formaldehyde. The VTi400 catalyst gives a one order of magnitude more intense 2ν(V=O) overtone at 2035 cm^{-1} than the VTi450 catalyst. This finding makes it possible to follow the adsorption-induced changes in the vanadyl groups.

Passing a 2% CH_2O + air mixture through an IR spectroscopic cell with VTi400 at 100°C gives rise to absorption bands at 1366, 1382, 1480, 1568, 1668, and 1724 cm^{-1} (Fig. 1). Similar bands result from CH_2O adsorption on VTiO450 [14]. The 1724 cm^{-1} band is due to the ν(C=O) vibrations in physically adsorbed CH_2O (SC 1 in Table 2). The weak absorption band at 1480 cm^{-1} is due to the $\delta(CH_2)$ vibrations in the dioxymethylene complex formed by CH_2O (SC 2). The $\nu_{as}(COO^-)$ = 1568 cm^{-1}, δ(CH) = 1382 cm^{-1}, and $\nu_s(COO^-)$ = 1366 cm^{-1} bands are typical of symmetrical bidentate formates on the surface (BF in Table 2).

The 1680 cm^{-1} band arises from the readsorption of the resulting formic acid. The same band was observed for formic acid adsorbed on both V–Ti catalysts [16]. It was assigned to the $\nu_{as}(COO^-)$ vibrations in the monodentate formate ion (MF in Table 2).

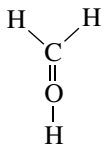
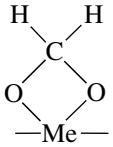
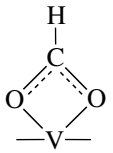
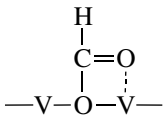
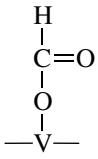
While the bands due to the SCs grow in intensity with increasing time on stream, the 2ν(V=O) = 2035 cm^{-1} band, which is due to the vanadyl groups of the catalyst, weakens (Fig. 1), indicating that these groups are involved in SC formation. (The 2ν(V=O) bands in Fig. 1a have a negative intensity, because the spectrum of the catalyst before formaldehyde adsorption was subtracted from the recorded spectrum.)

The weakly bound CH_2O (SC 1) and the dioxymethylene complexes (SC 2) show themselves in the IR spectrum at adsorption temperatures of 100°C and below. In the optimum catalysis temperature range (100–150°C), oxidized SCs, namely, BF and MF, are observed on the VTi400 surface.

The decomposition rate of BF depends on the presence of oxygen in the reaction mixture. This dependence was also observed for the VTi450 catalyst [14]. In the absence of oxygen, BF decomposes only above 150°C; in the presence of oxygen, it decomposes at a lower temperature of 100°C. The accelerating effect of oxygen on the decomposition of surface carbonate–carboxylate structures was also demonstrated in earlier works (see, e.g., [4, 5, 17]).

Aside from the above SCs, an asymmetric formate (AF in Table 2) forms on the VTi450 surface during formaldehyde oxidation. This complex gives rise to a $\nu_{as}(COO^-)$ = 1640 cm^{-1} absorption band [14]. The formation of this complex during the interaction between formaldehyde and the high-temperature catalyst VTi450 may be due to V_2O_5 resulting from the sintering of the sample, as is suggested by X-ray diffraction data [15]. A distinctive feature of AF is that its decomposition rate is independent of the presence of oxygen

Table 2. Surface compounds (SCs) identified by *in situ* IR spectroscopy in formaldehyde oxidation into formic acid on the VTiO400 and VTiO450 catalysts

SC*	SC structure	Absorption bands for VTiO450 [14], cm^{-1}	Absorption bands for VTiO400, cm^{-1}	Observation temperature, °C
SC 1		ν(O–H) = 3500 $\nu(CH_2)$ = 2786 ν(C=O) = 1728	ν(O–H) = 3500 $\nu(CH_2)$ = 2786 ν(C=O) = 1724	70
SC 2		$\nu_{as}(CH_2)$ = 2967 $\delta(CH_2)$ = 1480 $\omega(CH_2)$ = 1411	$\nu_{as}(CH_2)$ = 2967 $\delta(CH_2)$ = 1480 $\omega(CH_2)$ = 1411	70–100
BF		$\nu_{as}(COO^-)$ = 1568 $\nu_s(COO^-)$ =1366 δ(C–H) = 1380	$\nu_{as}(COO^-)$ = 1568 $\nu_s(COO^-)$ = 1366 δ(C–H) = 1382	70–150
AF		$\nu_{as}(COO^-)$ =1640	Is not formed	70–200
MF		Weak	$\nu_{as}(COO^-)$ = 1680	100–150

* MF, monodentate formate; BF, bidentate formate; and AF, asymmetric formate.

in the reaction mixture. AF decomposes at a measurable rate above 100°C.

The decomposition rates of BF and AF and the accumulation rates of formic acid and CO_x in the adsorption products are listed in Table 3. The accumulation rate of formic acid in the gas phase is close to the decomposition rate of BF in flowing air at 100°C and to the sum of the decomposition rates of BF and AF at 120 or 130°C.

The activation energy of BF decomposition is 28.8 kJ/mol and is similar to the activation energy of formic acid formation (28.4 kJ/mol) calculated from kinetic data for formaldehyde oxidation under steady-state conditions.

Analysis of the structures and reactivities of the surface intermediates on TiO_2 (anatase) [18] (which is inactive in formaldehyde oxidation) and the V–Ti catalysts suggests that vanadium sites are involved in formate formation.

We carried out SCF MO–LCAO *ab initio* calculations for a tetrahedrally coordinated surface V^{5+} cation (VO_4) as an active site (AS) of the V–Ti catalyst [19]. More specifically, the AS was modeled as a $V_2O_5OH_2$ cluster consisting of two oxygen-bridged VO_4 units. Each of these units has a V=O bond and a Lewis acid site (Scheme 1). The calculation has demonstrated that the bidentate formate ion results from the interaction between a formaldehyde molecule and a vanadyl oxygen atom (V=O), while the asymmetric formate ion results from the interaction between formaldehyde and bridging oxygen (V–O–V). These formates decompose to release formic acid to the gas phase, vacating surface AS's differing in the valence state of vanadium: V^{3+} results from the decomposition of BF; V^{4+}, from the decomposition of AF (Scheme 1). Since the AS in the case of BF decomposition has a lower valence (V^{3+}), it is reoxidized at a higher rate. It is apparently due to this

Table 3. Dissociation rate of surface compounds (w_{diss}) and accumulation rate of reaction products (w_{acc})

T, °C	$w_{diss} \times 10^{-15}$, molecules m^{-2} s^{-1}		$w_{acc} \times 10^{-15}$, molecules m^{-2} s^{-1}	
	BF	AF	HCOOH	CO_x
100	3.1	–	2.9	0.03
120	5.0	0.4	5.1	0.05
130	6.2	0.7	6.7	1.35

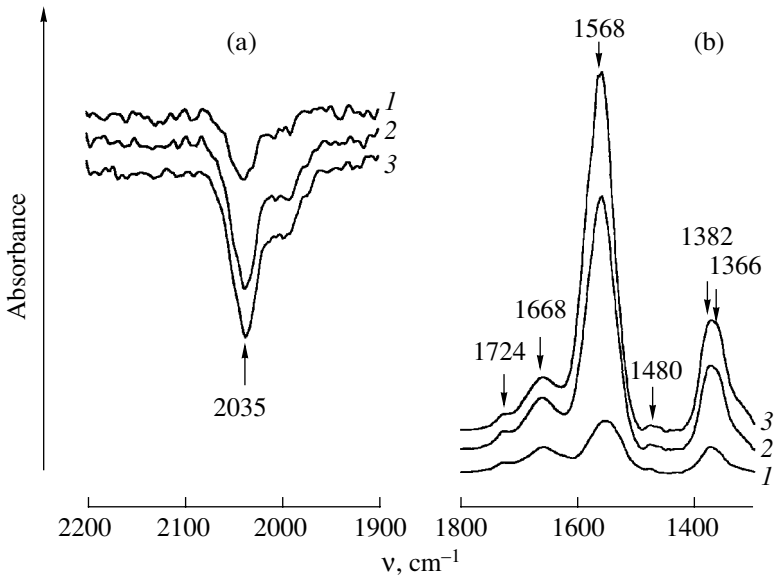
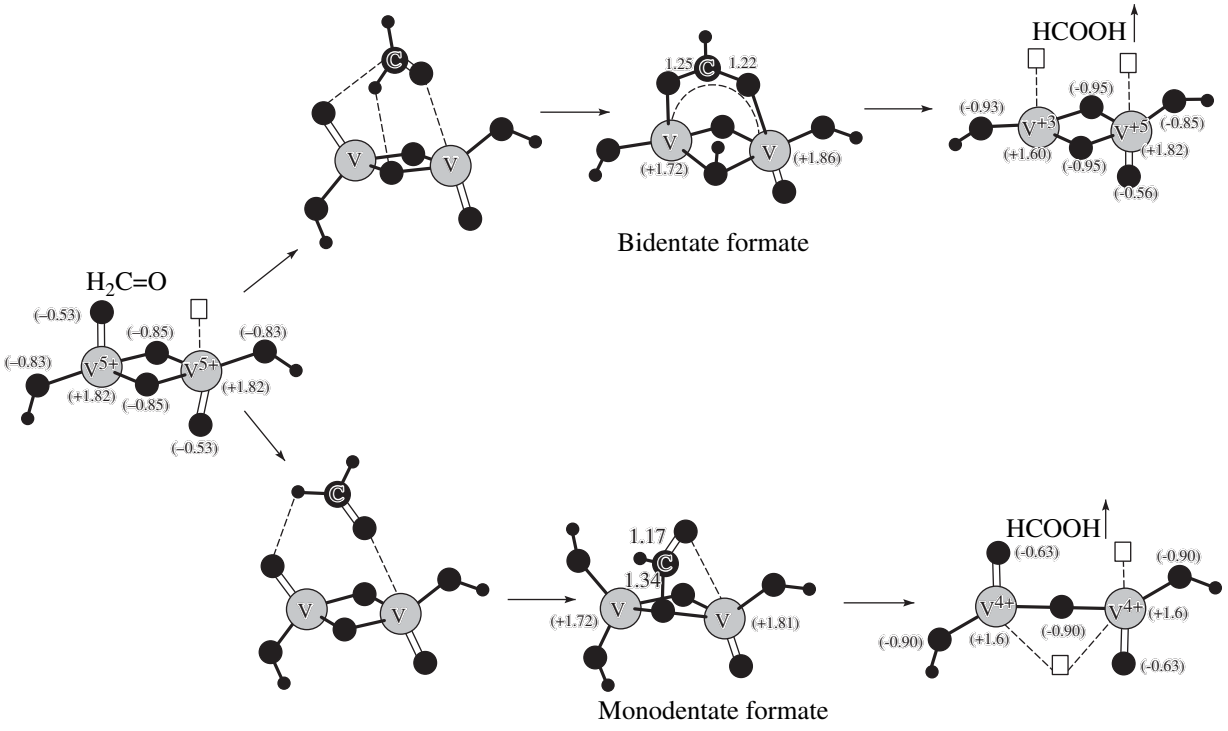


Fig. 1. IR spectra recorded for VTi400 at 100°C after a 2% HCHO + air mixture was passed through the reactor cell for (*1*) 50, (*2*) 100, and (*3*) 200 s. (a) Spectrum obtained by subtracting the spectrum of the original catalyst from the spectrum obtained after formaldehyde adsorption.

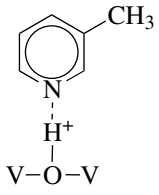
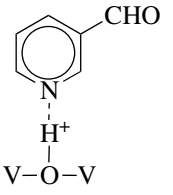
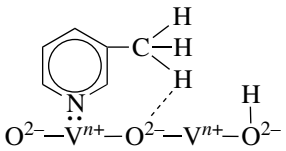
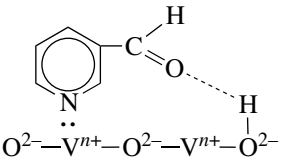
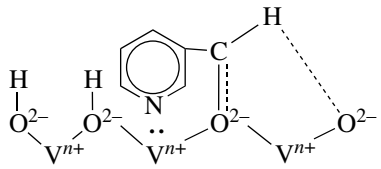
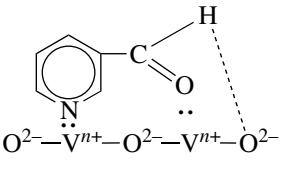
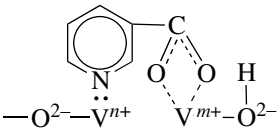
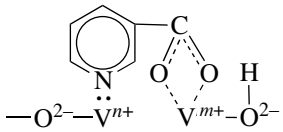
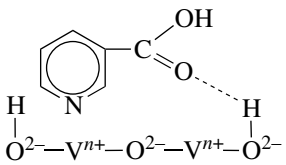
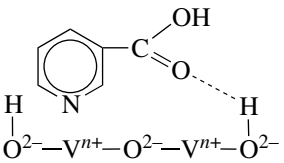
fact that the acid desorption step involves dioxygen by an association mechanism.

Thus, in the V_2O_5-containing two-phase system (VTi450), formic acid forms from BF and AF (Scheme 1). On the more finely dispersed catalyst (VTi400), formic acid forms by the first pathway (Scheme 1), through the decomposition of bidentate formates involving vanadyl groups.



Scheme 1. Formaldehyde conversion on the V–Ti–O catalyst. The calculated bond lengths are in Å; the parenthesized numbers are calculated atomic charges: V—vanadium atoms, ●—oxygen atoms, C—carbon atoms, ●—hydrogen atoms.

Table 4. Surface compounds (SCs) identified by *in situ* IR spectroscopy in 3-methylpyridine and 3-pyridinecarboxaldehyde oxidation into nicotinic acid on the V–Ti catalyst

SC	β-Picoline adsorption	Band assignment*			3-PyA adsorption	*T*, °C**
	SC structure	$C_5H_4NCH_3$ [21]	vibrations	C_5H_4NCHO [22]	SC structure	
SC1		1553 1632	≅N–H	1544		100–250
SC 2		1390 (1384) 1460 (1452) 1428 (1412) 1473 (1479) 1607 (1579) 1615 (1595)	$\sigma_s(CH_3)$ $\sigma_{as}(CH_3)$ ν(CC, CN) ν(CC, CN) ν(CC) ν(CC)	 1435 (1430) 1472 (1470) 1580 (1571) 1607 (1587)		100–150
			ν(C=O) ν(CH)(CHO) ν(CH) (ring)	1720 (1750) 2850 3075		
SC 3		1390 (1384) 1460 (1452) 1428 (1412) 1473 (1479) 1607 (1579) 1615 (1595) 1669 (1750)	$\sigma_s(CH_3)$ $\sigma_{as}(CH_3)$ ν(CC, CN) ν(CC, CN) ν(CC) ν(CC) ν(C=O)	 1435 (1430) 1472 (1470) 1580 (1571) 1607 (1587) 1670 (1750)		150–250
			ν(CH)(CHO) ν(CH) (ring)	2850 3075		
SC 4		1428 (1412) 1473 (1479) 1607 (1579) 1615 (1595) 1582 1420	ν(CC, CN) ν(CC, CN) ν(CC) ν(CC) $\nu_{as}(COO^-)$ $\nu_s(COO^-)$	1435 (1430) 1472 (1470) 1580 (1571) 1607 (1587) 1570 1417		200–300
SC 5			$C_5H_4NCHO_2$			250–300
		1428 (1430) 1473 (1480) 1607 (1571) 1615 (1587) 1748 (1780)	ν(CC, CN) ν(CC, CN) ν(CC) ν(CC) ν(C=O)	1435 (1430) 1472 (1480) 1580 (1571) 1607 (1587) 1740 (1780)		

* The numbers in parentheses are IR frequencies for individual compounds ($C_5H_4NCH_3$, C_5H_4NCHO, and $C_5H_4NCHO_2$).

** Temperature range in which the SC is observed.

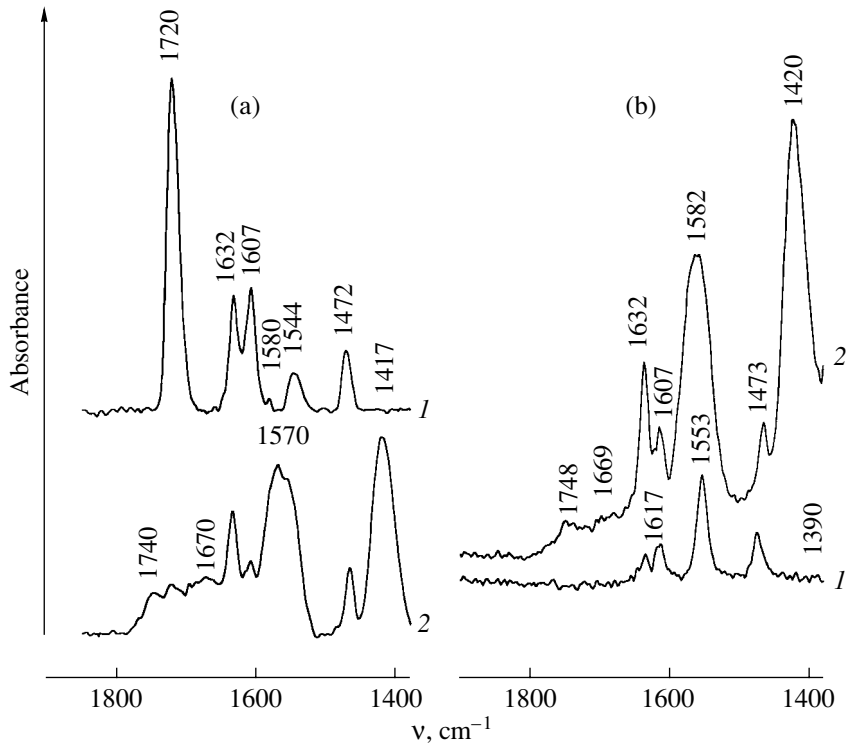
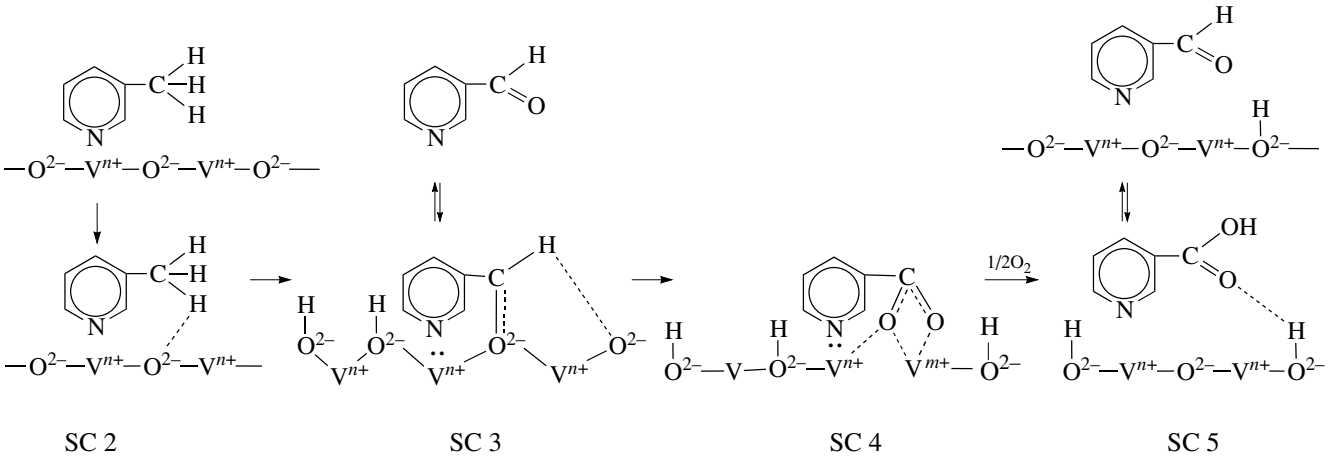


Fig. 2. IR spectra recorded for VTi450 at (*1*) 120 and (*2*) 250°C after 1 μl of (a) 3-pyridinecarboxaldehyde or (b) β-picoline was injected in the air flowing through the reactor cell.

β-Picoline oxidation on the V–Ti catalyst. We made an *in situ* FTIR spectroscopic study of the structure of the intermediates that form on the surface of the V–Ti catalyst during the oxidation of β-picoline and 3-pyridinecarboxaldehyde (3-PyA) into nicotinic acid. As follows from kinetic data [20], 3-PyA is an intermediate in β-picoline oxidation into nicotinic acid. Adsorption was carried out at 120°C by injecting β-picoline or 3-PyA (1–2 μl) into air or helium flowing at a rate of $V = 15$ ml/min through the reactor cell. (All feed pipelines were thermostated at 120°C.) Next, the cell, charged with the catalyst, was heated to 300°C at a rate of 5 K/min. The structures of intermediate compounds and the temperature ranges in which they were observed are presented in Table 4.

3-PyA adsorption. In the IR spectrum of 3-PyA adsorbed at 120°C (Fig. 2a), the normal mode of the ring is shifted by 3–12 cm^{-1} to higher frequencies, the ν(C=O) band of the CHO group is shifted by 30 cm^{-1} to lower frequencies, and there are new bands peaking at 1544 and 1633 cm^{-1}. The adsorption bands of the individual compounds and adsorbed 3-PyA are listed in Table 4. As is suggested by earlier data [21], the 1544 and 1633 cm^{-1} bands indicate that the N atom of the ring is protonated upon the interaction between 3-PyA and Brønsted acid sites (BASs) of the catalyst. Therefore, only molecular adsorbed 3-PyA species are detected on the V–Ti–O surface at 120°C, namely, protonated 3- PyA (SC 1) and a complex hydrogen-bonded through the carbonyl oxygen atom to a BAS and N-coordinated to a Lewis acid site (LAS) of the catalyst (SC 2). The structures and spectral properties of the SCs are presented in Table 4. Raising the temperature to 150°C reduces the proportion of the H-bonded complex (as indicated by a sharp weakening of the ν(C=O) = 1720 cm^{-1} band) and brings about a new ν(C=O) band at a lower frequency of 1670 cm^{-1} (see SC 3). These data suggest that elevating the temperature causes a stronger perturbation of the C=O bond in the CHO group of 3-PyA. Further raising the temperature to 300°C gives rise to new absorption bands at 1420 and 1580 cm^{-1}, which are characteristic of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ vibrations in surface carboxylates, and does not affect the intensity or position of the absorption bands due to the ring vibrations. Therefore, the 1420 and 1580 cm^{-1} bands should be assigned to the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ vibrations in surface nicotinates like SC 4 (Table 4).

Almost simultaneously with the formation of the nicotinates, a molecular adsorbed complex of nicotinic acid (SC 5) appears on the surface in the presence of oxygen gas, as is indicated by the absorption band at 1740 cm^{-1}. In the absence of oxygen, this band is not observed under similar adsorption conditions. In view of this, we attribute this band to nicotinic acid, which might be a product of nicotinate decomposition in the presence of oxygen gas.

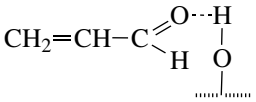
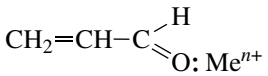
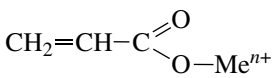
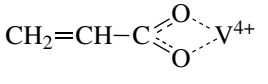
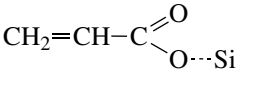


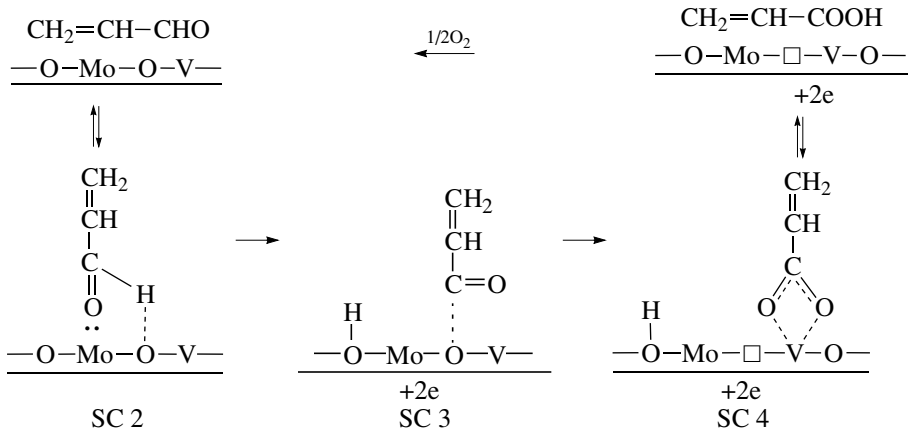
Scheme 2. β-Picoline and 3-PyA conversion on the V–Ti–O catalyst.

β-Picoline adsorption. Figure 2b shows the IR spectra of β-picoline adsorbed on the surface of the V–Ti–O catalyst at 120 and 250°C. The surface complexes forming in the course of β-picoline oxidation on the V–Ti catalyst are presented in Table 4.

At 120°C, β-picoline, like 3-PyA, binds through the nitrogen atom to an LAS of the catalyst to form the coordination compound SC 2 and to a BAS to form the 3-methylpyridinium ion SC 1. Raising the temperature to 150°C, brings about an absorption band at 1670 cm^{-1}, which is characteristic of ν(C=O) vibrations in adsorbed carbonyl compounds, and causes no effect on the absorption bands due to the ring vibrations. As is demonstrated above, similar bands are present in the IR spectrum of 3-PyA, suggesting that elevating the temperature causes oxidation of the methyl group into a carbonyl group in the adsorbed β-picoline to yield SC 3. As in the case of 3-PyA adsorption, this complex turns into the surface nicotinate SC 5 at 200–280°C in the presence of oxygen in the gas phase. We were unable to compare the decomposition rates of the nicotinates with the rate of accumulation of nicotinic acid in the gaseous desorption products because of the high sublimation temperature of the acid. Under our experimental conditions, between 200 and 280°C, nicotinic acid is partially readsorbed, as is indicated by a ν(C=O) = 1748 cm^{-1} band appearing in the IR spectrum. However, since the intensities of this band and the bands due

Table 5. Surface compounds (SCs) identified by *in situ* IR spectroscopy in acrolein oxidation into acrylic acid on the V–Mo–O/SiO_2 catalyst

SC	Structure	Band frequencies (cm^{-1}) and assignment	Observation temperature, °C
SC 1		ν(O–H) = 3500 ν(C=O) = 1690 ν(C=C) = 1625 σ(C–H) = 1370	25
SC 2		ν(C=O) = 1665 ν(C=C) = 1625 σ(C–H) = 1370	50–150
SC 3		ν(C=O) = 1725 ν(C=C) = 1625	50–150
SC 4		ν(C=C) =1625 $\nu_{as}(COO^-)$ =1520 $\nu_{s}(COO^-)$ = 1445	100–250
SC 5		ν(C=O) = 1750 ν(C=C) = 1620 σ(C–H) = 1420	150–300



Scheme 3. Acrolein conversion on the V–Mo–O catalyst.

to the nicotinate ($\nu_s(COO^-)$ = 1420 cm^{-1}; $\nu_{as}(COO^-)$ = 1570 cm^{-1}) vary in different ways with increasing temperature, it can be assumed that the surface nicotinates on the V–Ti catalyst decompose at catalysis temperatures to yield nicotinic acid.

Nicotinates on the V–Ti catalyst are observed at 200–300°C, in the temperature range of the selective oxidation of β-picoline and 3-PyA into nicotinic acid. β-Picoline or 3-PyA adsorption on the TiO_2 (anatase) surface gives no surface carboxylates in this temperature range. Therefore, vanadium ions are involved in the formation of nicotinic acid precursors in β-picoline or 3-PyA adsorption. This inference is supported by the fact that the V_2O_5 and V–Ti catalysts show a three orders of magnitude higher activity in β-picoline oxidation into nicotinic acid than TiO_2 [3].

Scheme 2 depicts the conversion of β-picoline and 3-PyA into nicotinic acid on the V–Ti–O catalyst. β-Picoline reacts with the LASs of the catalyst to form the coordination compound SC 2, which turns into the aldehyde-like complex SC 3 at 150–250°C and then into a nicotinate. 3-PyA also reacts with the LASs to give the coordination compound SC 3, which turns into a nicotinate at 150–250°C. The nicotinate is a direct precursor of nicotinic acid.

Acrolein oxidation on the V–Mo catalyst. The surface compounds forming during acrolein oxidation on the V–Mo catalyst were characterized by *in situ* IR spectroscopy [24, 25]. Between 100 and 300°C, we identified five surface complexes, namely, a hydrogen bonded compound (SC 1), a coordination compound (SC 2), a carbonyl-bonded compound (SC 3), an acrylate (SC 4), and acrylic acid readsorbed on SiO_2 (SC 5). The structures of these SCs are presented in Table 5.

Table 6. Dissociation rate of SCs (w_{diss}) and accumulation rate of gaseous desorption products (w_{acc})

T, °C	$w_{diss} \times 10^{-14}$, molecules $m^{-2}\,s^{-1}$			$w_{acc} \times 10^{-14}$, molecules $m^{-2}\,s^{-1}$	
	SC 2	SC 4	SC 5	acrylic acid	CO_x
125	4.5	0.4	–	0.5	–
190	–	0.6	0.3	1.1	0.03
230	–	1.0	1.4	2.7	0.08

Table 6 lists the decomposition rates of the SCs and the accumulation rates of gaseous desorption products (acrylic acid and CO_x). At a desorption temperature of 125°C, the decomposition rate of the acrylate (SC 4) is close to the accumulation rate of acrylic acid. At higher temperatures, when readsorbed acid (SC 5) is also present on the catalyst surface, the accumulation rate of acrylic acid is close to the sum of the decomposition rates of SC 4 and SC 5.

It follows from the above results that the acrylate SC 4 is an intermediate in the formation of acrylic acid.

It was demonstrated by successive adsorption of acrolein and a test substance (NO) that the centers stabilizing the acrylate (SC 4) are V^{4+} ions [24, 25]. The formation of acrylic acid involves oxygen of the catalyst and proceeds by a redox mechanism [26].

Scheme 3 shows how acrolein on the surface of the V–Mo–O catalyst is converted via coordinated acrolein and a carbonyl-bonded complex into an acrylate and, then, acrylic acid.

CONCLUSIONS

The study of surface intermediates on the vanadium-containing (V–Mo and V–Ti) oxide catalysts demonstrated that formaldehyde oxidation into formic acid, acrolein oxidation into acrylic acid, and β-picoline and 3-pyridinecarboxaldehyde oxidations into nicotinic acid proceed by the same mechanism. This mechanism includes the following steps: (1) formation of molecularly bonded compounds through the interaction between a high-electron-density atom of the original molecule (O in the aldehydes and N in β-picoline and 3-pyridinecarboxaldehyde) and an AS of the catalyst;

(2) heterolysis of the C–H bond in the CHO group of the aldehyde or in the CH_3 group of β-picoline; (3) oxidation of the hydrocarbon fragment, accompanied by the reduction of the AS, and interaction between the oxidized fragment and catalyst oxygen, yielding surface carboxylates (formates, acrylates, or nicotinates); and (4) catalyst reoxidation by a redox mechanism as a separate step (in the case of acrolein oxidation on the V–Mo–O catalyst) or by an association mechanism as part of the oxygen adsorption–acid desorption step (in the case of formaldehyde or 3-pyridinecarboxaldehyde oxidation on the V–Ti–O catalyst).

The surface intermediates—formates, acrylates, and nicotinates—are fixed on vanadium ions. These saltlike surface compounds are the direct precursors of the acids. The coincidence of the kinetics of carboxylate decomposition and acid formation suggests that these reactions are controlled by the carboxylate decomposition step.

Carboxylate decomposition without destruction of the carbon skeleton is possible only if the acid moiety is weakly bound to the AS of the catalyst.

Vanadium, a unique component of oxide catalysts for selective oxidation, has been discussed in the literature as an element whose reduced states have acid–base properties optimal for the formation of weakly bonded saltlike compounds [27, 28].

Electrons are transferred from the substance oxidized to the catalyst in the oxidation step of the catalytic cycle, so the resulting SC is fixed on the reduced AS. For acrolein oxidation, it was demonstrated experimentally that these ASs are surface V^{4+} cations [21, 22]. For formaldehyde oxidation, it was shown by calculations that the formate ions are bound to V^{3+} and V^{4+} [19].

Due to their weak acidic properties, the surface cations V^{3+} and V^{4+} ensure optimal binding between the carboxylates and the catalyst surface and, as a consequence, dissociation of these complexes without destruction of the carbon skeleton in the catalytic reaction.

The effectiveness of vanadium as the key component of mixed oxide catalysts for oxidation of organic compounds into carboxylic acids is also demonstrated in other studies [2, 4–8]. The participation of saltlike surface compounds (benzoates stabilized on the vanadium ions of a V–Sn–O catalyst) in the formation of benzoic acid was first reported in [5]. Benzoate ions stabilized on vanadium cations are also viewed as intermediates in toluene oxidation into benzoic acid [4]. Reduced vanadium (V^{4+}) is believed to be necessary for selective and active catalysis in butene oxidation into acetic acid [2].

Thus, the intermediates in acid formation are saltlike surface compounds, specifically, carboxylates. These intermediates are stabilized on vanadium cations. The dissociation of the $RCOO^{-}V^{n+}$ surface complexes is the rate-limiting step in carboxylic acid formation. Owing to the reduced state of vanadium (V^{4+} and V^{3+}), the carboxylate ions are weakly bound and the surface complexes dissociate so that their carbon skeleton is intact, ensuring selectivity of the oxidation.

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