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Heterogeneous Selective Oxidation of Formaldehyde on Oxide Catalysts: *In situ* FTIR Study of Formaldehyde Surface Species on a V–Ti–O Catalyst and Oxygen Effect

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Abstract—The interaction of formaldehyde with a highly selective V–Ti–O catalyst for the oxidation of formaldehyde to formic acid is studied by Fourier-transform infrared (FTIR) spectroscopy at 70–200°C. In a flow of formaldehyde/oxygen mixture and in a mixture without oxygen at optimal temperatures for formic acid formation (100–140°C), methoxy groups and other oxygenates are formed in small amounts. These are two bidentate formates and covalently bound monodentate formate. The fact that similar oxygenates are observed independently of the presence of oxygen in the reaction mixture suggests the participation of the catalyst oxygen in their formation. Oxygen accelerates the desorption of bidentate formates. Bidentate formates of one type decompose in a flow of air at 100–150°C, and bidentate formates of the other type decompose at 170–200°C.

INTRODUCTION

Formaldehyde is one of the key substances in the catalytic organic synthesis. It is the main product of the selective methanol oxidation and an intermediate in alcohol synthesis from syngas, methanol decomposition, and methyl formate synthesis from methanol. We have shown that formaldehyde is oxidized to formic acid with a high selectivity on vanadium–titanium oxide catalysts [1]. Formaldehyde adsorption on oxide catalysts was studied by IR spectroscopy [2–21]. Depending on the chemical nature of the catalyst and reaction conditions, various surface species are formed: coordinatively bound formaldehyde on Al_2O_3 [2], formates on ZnO, Al_2O_3, TiO_2, Fe_2O_3, ZrO_2, V–Ti–O, and many other oxide catalysts [2–21], dioxymethylene and polyoxymethylene complexes on MgO and TiO_2 [10, 11, 18] and methoxy on TiO_2, Fe_2O_3, ZrO_2, and CeO_2 [2, 18]. No such studies have been carried out under the conditions of formaldehyde oxidation to formic acid.

The goal of this work was to study *in situ* the surface species formed under the conditions of formaldehyde oxidation to formic acid over a highly selective V–Ti oxide catalyst by Fourier-transform infrared (FTIR) spectroscopy. A mechanistic and kinetic study [22] has shown that oxygen substantially affects the rate of formic acid formation. We took this into account and gave special attention to the effect of oxygen on the forms of formaldehyde adsorption and reactivity.

EXPERIMENTAL

A vanadium–titanium oxide catalyst contained 20 wt % V_2O_5 and 80 wt % TiO_2. It was prepared by mixing anatase TiO_2 and vanadyl oxalate with further thermal treatment in air as described in [1]. The specific surface area was 26 m^2/g.

For *in situ* IR studies, we used a BOMEM MB-102 Fourier-transform IR spectrometer and a flow-type high-temperature cell as a reactor, analogous to that described in [23]. The cell volume was 1.5 cm^3. A catalyst tablet (1 × 3 cm and ~50 mg) was placed into the cell. Before each run, the tablet was trained in the cell for an hour in a flow of air at 250°C. Then, the cell with the catalyst sample was cooled to a desired temperature, and the air flow was replaced by the flow of a formaldehyde-containing mixture. The gaseous mixture was supplied at a rate of 150 ml/min. The mixtures of the following composition were used: 2 vol % CH_2O in air (CH_2O + O_2) and 2 vol % CH_2O in helium (CH_2O + He). Before the supply of CH_2O + He, the sample was purged with helium for 20 min. Formaldehyde was prepared by the thermal decomposition of a paraform. All gas pipes before and after the cell were kept at a constant temperature to prevent formaldehyde polymerization and product condensation. IR spectra were recorded at time intervals. Each spectrum was recorded for 45 s (10 scans). The spectra thus obtained were a superposition of the spectra of the catalyst and surface species. To isolate the spectra of surface species, background catalyst spectra recorded before the supply of a formaldehyde-containing mixture into a cell were subtracted from those measured after the supply. Overlapping signals were separated using an SK-2 curve synthesizer.

The gas phase was analyzed by chromatography and FTIRS in an IR cell placed immediately after the reac-

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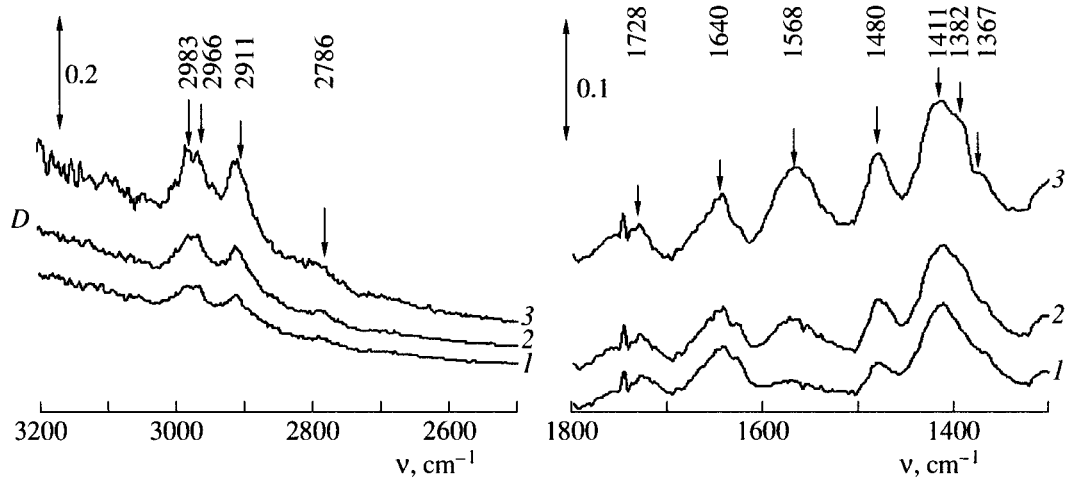


Fig. 1. FTIR spectra of surface species at 70°C observed when the $CH_2O + O_2$ mixture passes through the cell/reactor for (*1*) 40, (*2*) 320, and (*3*) 1800 s.

tor/cell. The IR spectra of the gas phase were recorded in either parallel runs or in turns. In the latter case, the gas cell and reactor/cell were placed into the instrument in turns. For quantitative measurements we chose the *R*-branch of the absorption band νCO at 2110 cm^{-1} for carbon monoxide, the Q-branches of the νC=O band at 1744 cm^{-1} for formaldehyde and the νC–O band at 1105 cm^{-1} for formic acid, which does not overlap with the bands of gaseous formaldehyde. The extinction coefficients of these bands were determined using calibrating gaseous mixtures of a known concentration.

RESULTS AND DISCUSSION

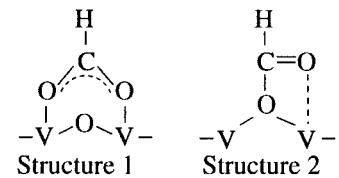
Formaldehyde Adsorption

The following absorption bands appeared in the first spectrum recorded at 70°C after 40 s from the start of the $CH_2O + O_2$ supply into the cell: 3370, 2983, 2966, 2911, 2786, 1728, 1640, 1568, 1480, 1411, 1380, and 1360 cm^{-1}. The IR spectra recorded at different intervals are shown in Fig. 1. With an increase in the contact time, the intensities of absorption bands increase and reach stationary values after about 30 min. The table describes the assignment of absorption bands.

The frequencies 2983 and 2911 (νCH_2), 1481 (δCH_2), and 1434 (ωCH_2) cm^{-1} are typical of polyoxymethylene [24], and frequencies 2966 (νCH_2), 2786 ($2\omega CH_2$), 1480 (δCH_2) and 1411 (ωCH_2) cm^{-1} are typical of dioxymethylene complexes [25, 26].

IR bands at 1728 and 2786 cm^{-1} are characteristic of C=O and C–H vibrations in the aldehyde CHO group [25]. A similar change in the intensity of absorption bands at 1728 cm^{-1} (νC=O) and 3370 cm^{-1} (νO–H of the catalyst) during adsorption and desorption and a lowered frequency νC=O compared to vibrations in the gas-phase aldehyde molecule [25] point to the formation of a hydrogen-bound formaldehyde complex.

The bands $\nu_{as}COO^-$ at 1640 and 1568 cm^{-1} and the band ν_sCOO^- at 1360 cm^{-1} are typical of surface formates [17] (see the table). The presence of two $\nu_{as}COO^-$ bands in the IR spectrum points to the formation of two nonequivalent formates. The bands $\nu_{as}COO^-$ = 1568 cm^{-1} and ν_sCOO^- = 1360 cm^{-1} are characteristic of bidentate formates, which will be denoted as BF (structure 1) throughout the paper. The ν_sCOO^- band for the second formate conjugated with $\nu_{as}COO^-$ = 1640 cm^{-1} is absent from the observable region (above 1300 cm^{-1}) of the IR spectrum. This means that this band is below 1300 cm^{-1}. Such positions of IR bands are characteristic of formates with more covalent bonds (structure 2). The structure of this complex is closer to the monodentate formate (MF). In this complex, the frequency ν_sCOO^- should be lower than 1300 cm^{-1}, and an increase in the multiplicity of the C=O bond leads to an increase in $\nu_{as}COO^-$ to 1640 cm^{-1}.



Structure 1 Structure 2

Figure 2 shows the IR spectra of surface compounds recorded at 70°C at different time intervals when the CH_2O + He mixture passes through the cell. Similarly to the case when oxygen is present in the flow, IR spectra contain the bands belonging to hydrogen-bound formaldehyde (νC=O = 1728 cm^{-1}), adsorbed BF ($\nu_{as}COO$ = 1568 cm^{-1}, δC = 1380, and ν_sCOO^- = 1360 cm^{-1}) and MF ($\nu_{as}COO^-$ = 1640 cm^{-1})

The adsorption from the CH_2O + He mixture leads to a lower concentration of dioxymethylene complexes, which is evident from the low intensity of the IR band at 1411 cm^{-1} that is most characteristic of this complex

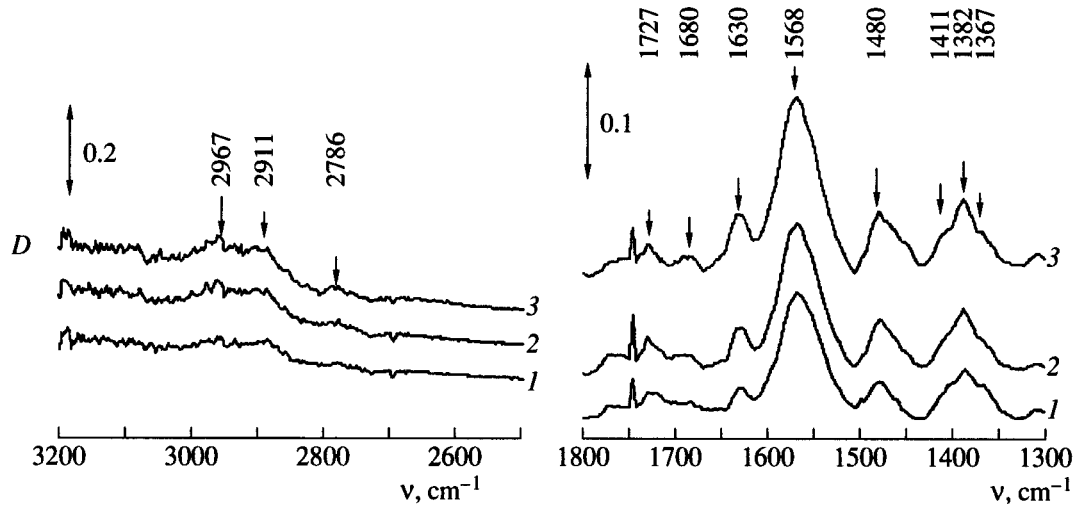


Fig. 2. FTIR spectra of surface species at 70°C observed when the CH_2O + He mixture passes through the cell/reactor for (*1*) 320, (*2*) 900, and (*3*) 1800 s.

(Fig. 2). In addition, a new nonintense band νC=O = 1680 cm^{-1} appears in the spectrum. Taking into account a stronger shift toward the low-frequency region as compared to the frequency of vibrations associated with the H-bound formaldehyde, this band can be assigned to νC=O for formaldehyde coordinatively bound to à Lewis acid site via carbonyl oxygen.

Effect of Temperature on the Transformations of Surface Species

Figures 3 and 4 show the IR spectra recorded at different temperatures 30 min after the start of $CH_2O + O_2$ and CH_2O + He admission. An increase in temperature to 100°C results in the disappearance of IR bands corresponding to hydrogen-bound formaldehyde (1728 cm^{-1}), dioxymethylene and polyoxymethylene complexes (2983, 2966, 2911, 2786, 1480, and 1411 cm^{-1}). As this takes place, weak IR bands appear at 1478 and 1447 cm^{-1} (Figs. 3 and 4, spectrum *2*), which are characteristic of surface methoxy groups CH_3O^- (see the table). As the temperature is increased from 150 to 190°C, the maximum of the $\nu_{as}COO^-$ band shifts from 1568 to 1560 cm^{-1}. This points to a change in the BF state. We will further denote bidentate formate formed at temperatures below and above 150°C by BF-1 and

Spectral characteristics of formaldehyde adsorption products on the V–Ti oxide catalyst

IR band assignment	Vibration frequencies, cm^{-1}					
	IR band of adsorption products	CH_2O (gas) [25]	dioxymethylene [25, 26]	polyoxymethylene [24]	formates $HCOO^-$ [17]	methoxy CH_3O^- [17]
$\nu_{as}CH_2$	2983, 2966	2843	2945	2984	–	–
$\nu_{as}CH_3$	–	–	–	–	–	2965
ν_sCH_3	–	–	–	–	–	2935
$2\delta CH_2$	–	–	2932	–	–	–
νCH	–	–	–	–	2905–2850	–
ν_sCH_2	2911, 2786	2783	2882	2920	–	–
$2\omega CH_2$	–	–	2770	–	–	–
νC=O	1728, 1680	1746	–	–	–	–
$\nu_{as}COO$	1640, 1560–1568	–	–	–	1600–1550	–
δCH_2	1478	1500	1473	1471	–	–
$\delta_{as}CH_3$	1480	–	–	–	–	1452
δ_sCH_3	1443	–	–	–	–	1438
δCH^+, ν_sCOO	1380, 1366	–	–	–	1410–1350	–
ωCH_2	1434, 1411	1249	1401	1434, 1384	–	–

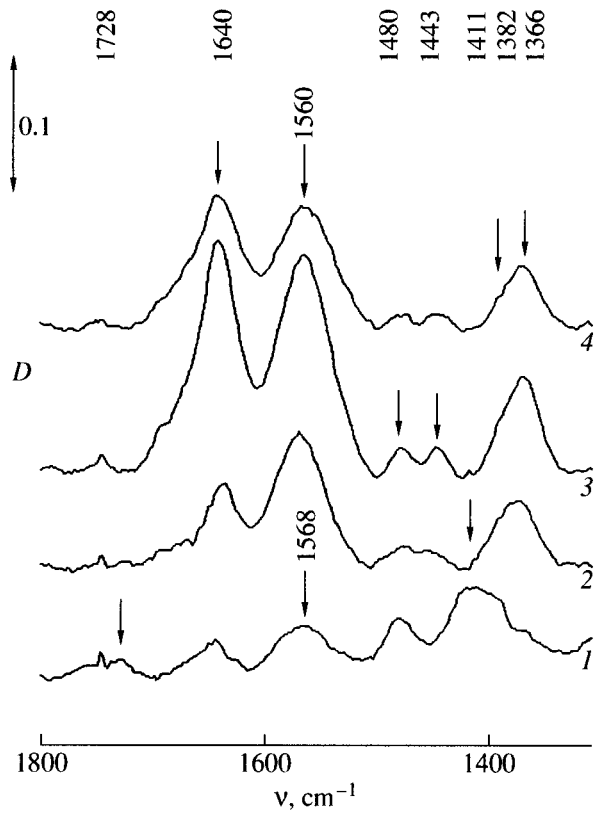


Fig. 3. FTIR spectra of surface species under steady-state conditions observed when the $CH_2O + O_2$ mixture passes through the cell/reactor at (*1*) 70, (*2*) 100, (*3*) 150, and (*4*) 190°C.

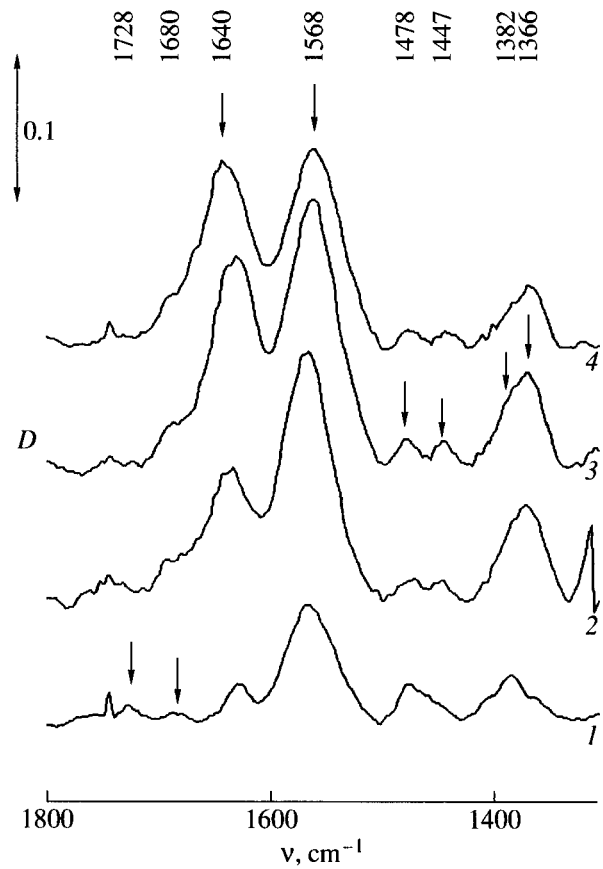


Fig. 4. FTIR spectra of surface species under steady-state conditions observed when the CH_2O + He mixture passes through the cell/reactor at (*1*) 70, (*2*) 120, (*3*) 150, and (*4*) 190°C.

BF-2, respectively. The difference between BF-1 and BF-2 is in the $\nu_{as}COO^-$ frequency ($\Delta = 8$ cm^{-1}). As will be shown below, they also differ in thermal stabilities.

Figure 5 shows the temperature effect on the steady-state concentrations of gaseous products of formaldehyde conversion (formic acid and CO) and on the extinction of the characteristic IR bands, which are proportional to the corresponding surface coverages when $CH_2O + O_2$ and CH_2O + He mixtures pass through the reactor: BF (1568 and 1560 cm^{-1}), MF (1640 cm^{-1}), methoxy (1447 cm^{-1}), dioxymethylene (1411 cm^{-1}), and polyoxymethylene (1480 cm^{-1}).

At 70–140°C, the main product of formaldehyde oxidation is formic acid. In the presence of oxygen, the concentration of formic acid is almost an order of magnitude higher (Fig. 5, curve *1*) than in the absence of oxygen (Fig. 5, curve *2*). The concentration of formic acid passes through a maximum at ~150°C both with and without O_2. A decrease in the concentration of acid at temperatures higher than 150°C is associated with the consecutive decomposition of formic acid into CO and water [1]. Both in helium-containing and oxygen-containing mixtures at 170–200°C, carbon monoxide (Fig. 5, curves *3* and *4*) and water dominate in the products.

The surface concentrations of BF, MF, and methoxy also pass through maxima at ~150°C both in the presence and in the absence of oxygen in the reaction mixture. The surface concentrations of BF are higher in the case of the CH_2O + He mixture.

Thermal Stability of Surface Complexes

The decomposition of surface complexes was carried out at 70–200°C. The CH_2O + He and $CH_2O + O_2$ mixtures were replaced by air and helium after reaching the steady-state surface coverages. The IR spectrum of air and helium under the conditions of desorption 100°C, miss the bands for hydrogen-bound and coordinatively-bound formaldehyde, dioxymethylene, and polyoxymethylene. At 150°C, the IR bands for methoxy groups also disappear. The extinction at 1640 cm^{-1} is proportional to MF coverage and decreases slightly at 100–150°C during desorption in both oxygen and helium and substantially at temperatures higher than 150°C.

The presence of oxygen in the reaction mixture substantially affects the rate of BF desorption.

Figure 6 shows how the intensity of the IR band at 1568–1560 change with time at different temperatures.

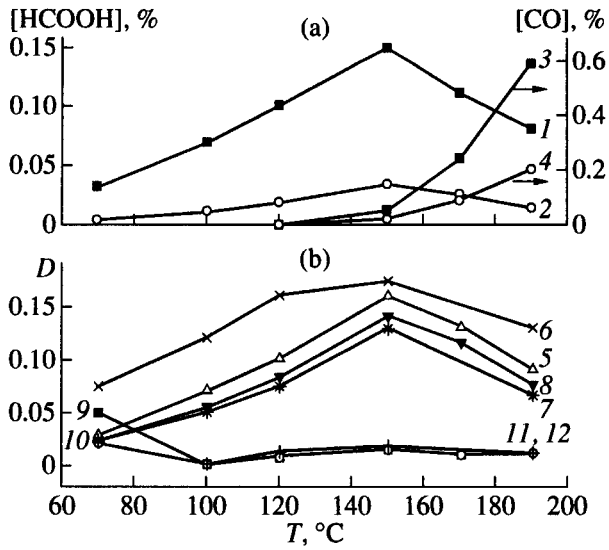


Fig. 5. Dependences of (a) steady-state concentrations of formic acid and CO in the gas phase at the outlet of the cell/reactor and (b) extinctions on the temperature when the mixtures $CH_2O + O_2$ and CH_2O + He pass through the cell/reactor: (*1*) [HCOOH] and $CH_2O + O_2$; (*2*) [HCOOH] and CH_2O + He; (*3*) [CO] and $CH_2O + O_2$; (*4*) [CO] and CH_2O + He; (*5*) *D* for 1568–1560 cm^{-1} and $CH_2O + O_2$; (*6*) *D* for 1568–1560 cm^{-1} and CH_2O + He; (*7*) *D* for 1640 cm^{-1} and $CH_2O + O_2$; (*8*) *D* for 1640 cm^{-1} and CH_2O + He; (*9*) *D* for 1411 cm^{-1} and $CH_2O + O_2$; (*10*) *D* for 1411 cm^{-1} and CH_2O + He; (*11*) *D* for 1447 cm^{-1} and $CH_2O + O_2$; (*12*) *D* for 1447 cm^{-1} and CH_2O + He.

Curves *9* and *10* refer to temperatures lower than 100°C, and curves *11* and *12* refer to temperatures between 100 and 190°C.

The intensity of this band is proportional to the BF-1 and BF-2 coverages upon replacing the $CH_2O + O_2$ mixture by air (Fig. 6a) and helium (Fig. 6b). The relative intensity (D^*) of these bands when steady-state coverages are achieved is taken to be unity. As can be seen from Fig. 6a, the replacement of the reaction mixture by air results in a substantial decrease in the BF coverage. If the reaction mixture is replaced by helium, these changes are small at all temperatures (Fig. 6b).

DISCUSSION

Formaldehyde oxidation to formic acid on the V–Ti oxide catalyst occurs with a high selectivity at 100–140°C. At higher temperatures, the selectivity to formic acid decreases due to its decomposition into CO and water [1]:

$$CH_2O \longrightarrow HCOOH \longrightarrow CO + H_2O.$$

The measurements in the IR cell/reactor show that formic acid is formed even at 70°C and its concentration increases with an increase in the temperature to 150°C. As can be see from Fig. 5, the concentration of formic acid in the $CH_2O + O_2$ run is about an order of magnitude higher than in the CH_2O + He run. At 150°C, CO appears in the reaction products. A further increase in temperature results in a decrease in the concentration of formic acid and an increase in the concentration of CO. IR measurements in the cell/reactor with the same catalyst loading under analogous conditions showed that the same species are formed on the surface independently of the presence of oxygen in the reaction mixture. These are hydrogen-bound formaldehyde, dioxymethylene, polyoxymethylene, methoxy (CH_3O^-), and formates (BF-1, BF-2, and MF). Hydrogen-bound formaldehyde, dioxymethylene, and polyoxymethylene are formed under the conditions of adsorption at 100°C (Figs. 1–4) and readily desorb in the flow of helium or air at 70–100°C. Figures 1 and 2 show that the intensity of the absorption band at 1411 cm^{-1} of dioxymethylene and its concentration are higher when oxygen is present in the reaction mixture. Because dioxymethylene is formed by the nucleophilic attack of surface oxygen on the positively charged carbon atom of the carbonyl group [2], their formation in the presence of oxygen is due to the high oxygen coverage under these conditions. At 100°C, the IR bands of dioxymethylene and polyoxymethylene disappear when either mixture is used, but the formate bands become more intense (Figs. 3 and 4). This fact suggests that methoxy groups, and some portion of formates are formed from these surface complexes. The disproportionation of dioxymethylene to form surface formates and methoxy groups has also been observed in the study of formaldehyde adsorption on MgO [10, 11], TiO_2 [28], and some other oxide catalysts [2].

MF was formed during the adsorption of formaldehyde at all temperatures. The intensity of the band at 1640 cm^{-1}, which is proportional to the surface concentrations of MF, are comparable when oxidative and reductive mixtures are used (Fig. 5). MF is stable under the conditions of formaldehyde oxidation. When the reaction mixture is replaced by air or helium, the concentration of MF slightly decreases. The band at 1640 cm^{-1} disappears from the IR spectrum after sample heating for 3 min at 220°C.

BF coverages are substantially higher in the case of the CH_2O + He mixture than in the case of $CH_2O + O_2$ (Fig. 5, curves *5* and *6*). The thermal stabilities of BF-1 and BF-2 are substantially different during desorption in air or helium. As can be seen from Fig. 6b, under the conditions of desorption in helium at 70–190°C, only a slight change in the BF coverage is observed. BFs start to decompose at a noticeable rate in the helium flow only at temperatures higher than 150°C. In the oxygen flow, BF-1 decomposes at a measurable rate at 100°C (Fig. 6a). The extinction at the maximum between 1570–1560 cm^{-1} changes as a function of time recorded after the replacement of the reaction mixture by air. It can be linearized in the first-order coordinates ($\ln(D_{st}/D) = f(t)$). This enabled us to obtain the rate constants of desorption (k_{des}, s^{-1}) at the corresponding temperatures. The Arrhenius plots of BF desorption rate constants has a break point at 150°C (Fig. 7). The

activation energy is 28.4 kJ/mol at 100–150°C and 103.2 kJ/mol at 150–190°C. These data point to the formation two surface complexes with different thermal stabilities. As shown above, at temperatures higher than 150°C, the adsorption state of BF-1 changes, which is reflected in a shift of the maximum of the $\nu_{as}COO^- = 1568$ cm^{-1} band toward a lower-frequency region of the IR spectrum. At 170 and 190°C, the maximum is at 1560 cm^{-1}. These changes may be due either to the migration of BF-1 along the surface to stronger sites or to the re-adsorption of formic acid on these sites.

Thus, oxygenates (MF, BF-1, and BF-2) are formed under the conditions of formaldehyde transformation on the V–Ti oxide catalyst surface. The appearance of similar oxidized complexes in the presence and absence of oxygen points to the participation of catalyst oxygen in their formation. A lower coverage by BF in the oxidative mixture is explained by the higher rate of their decomposition in the presence of oxygen in the gas phase.

Comparison of the results of catalytic and spectral studies suggests that BF-1 is an intermediate in the formation of formic acid. The activation energies of formic acid and CO formation calculated using the results of steady-state catalytic experiments in IR cell/reactor are 28.8 and 109.2 kJ/mol. According to the results of kinetic data obtained in the study of formaldehyde oxidation on the V–Ti oxide catalyst, these values are 28.4 and 108.1 kJ/mol, respectively [22]. Assuming that the rate-limiting step is the decomposition of surface complex, the coincidence of activation energies of formic acid formation (28.8 kJ/mol) and BF-1 decomposition (28.4 kJ/mol) may serve as evidence of the formation of formic acid from BF-1. The formation of BF-1 at optimal temperatures for the formation of formic acid (100–140°C) and the acceleration of BF-1 decomposition and formic acid formation by oxygen point to the same fact. Analogously, BF-2 can be an intermediate in the oxidation of formaldehyde to CO. BF-2 appears at temperatures below 150°C, where the reaction is not selective and leads to the formation of CO. The activation energy of BF-2 decomposition (103.2 kJ/mol) is close the activation energy of CO formation (108.1 kJ/mol) [22].

Formate species are formed on the surfaces of many oxide catalysts in the water-gas shift reaction, methanol synthesis, formic acid decomposition, and hydrocarbon, alcohol, aldehyde, and acid oxidation [23]. Analysis of the literature data shows that the rate of formate decomposition and pathways of conversion depend on the composition of the reaction medium. The gaseous products of formate thermal decomposition in the absence of gas-phase additives are usually CO and water (or hydrogen). In the presence of hydrogen, formates are hydrogenated to form methoxy groups over the catalysts for methanol synthesis. Methoxy groups then decompose to form methanol [29]. Busca *et al.* [15] showed that, under the conditions of methanol oxidation on V–Ti oxide catalysts, formates react with gaseous methanol to form methyl formate. In this work, we conjecture the participation of formates in the formation of formic acid if water vapors are present in the reaction mixture. We showed that, on the V–Ti oxide catalyst, bidentate formates are decomposed at 100–140°C in the presence of oxygen to form formic acid, which is evolved into the gas phase.

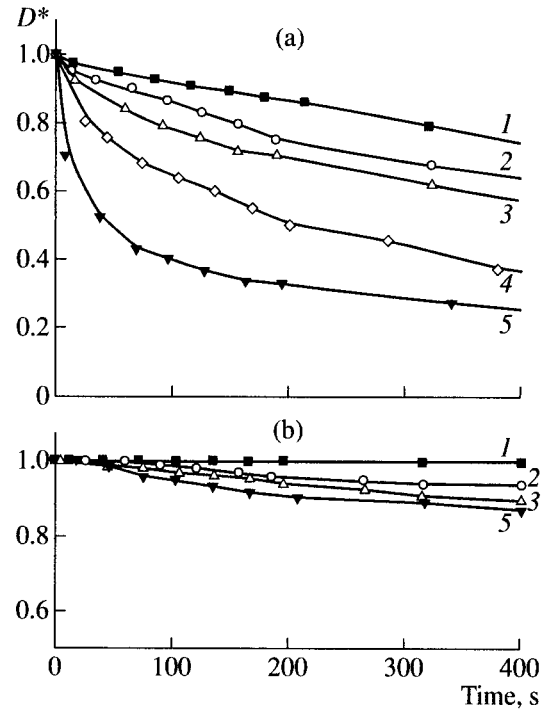


Fig. 6. A change in the normalized extinction at the maximum of the band at 1568–1560 cm^{-1} when the reaction mixture ($CH_2O + O_2$) is replaced by (a) air and (b) helium at (*1*) 100, (*2*) 120, (*3*) 150, (*4*) 170, and (*5*) 190°C.

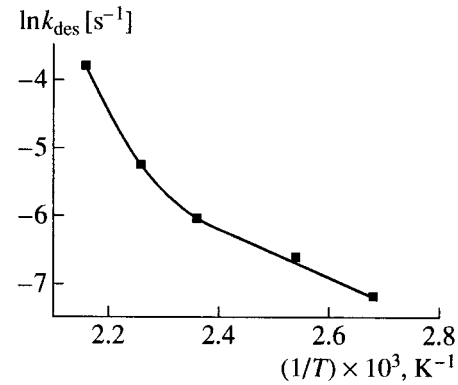


Fig. 7. The Arrhenius plot of the rate constant of BF desorption.

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