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In situ FTIR Study of the Adsorption of Formaldehyde, Formic Acid, and Methyl Formiate at the Surface of TiO_2 (Anatase)

G. Ya. Popova, T. V. Andrushkevich, Yu. A. Chesalov, and E. S. Stoyanov

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

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Abstract—The catalytic properties of TiO_2 (anatase) in the reactions of formaldehyde oxidation and formic acid decomposition are examined. At 100–150°C, formaldehyde is converted into methyl formate with high selectivity regardless of the presence of oxygen in the reaction mixture. Formic acid is decomposed to CO and water. Surface compounds formed in the reactions of formaldehyde, formic acid, and methyl formate with TiO_2 (anatase) are identified by *in situ* FTIR spectroscopy. In a flow of a formaldehyde-containing mixture at 100°C, H-bonded HCHO, dioxymethylene species, bidentate formate, and coordinatively bonded HCHO are observed on the TiO_2 surface. In the adsorption of formic acid, H-bonded HCOOH and two types of formates (bidentate and unsymmetrical formates) are formed. In the adsorption of methyl formate, H-bonded $HCOOCH_3$, $HCOOCH_3$ coordinatively bonded via the carbonyl oxygen, and bidentate formate are identified.

INTRODUCTION

Different modifications of TiO_2 (anatase and rutile) are widely used as supports in the preparation of V–Ti–O catalysts for selective hydrocarbon oxidation [1–3], in particular, formaldehyde oxidation to formic acid [4] and methanol oxidation to methyl formate [5].

Data on the catalytic and adsorption properties of TiO_2 in formaldehyde conversion reactions are scarce. Cheng [6] found that, on TiO_2 (anatase) in a formaldehyde–air atmosphere, methyl formate, methanol, and carbon oxides were the reaction products at 190°C, whereas these were methanol, carbon oxides, and dimethyl ether at 300°C. In the oxidation of formaldehyde on TiO_2 in the presence of water vapor at 275°C, the formation of methyl formate, methanol, carbon oxides, and small amounts of formic acid was observed [7].

The surface compounds of formaldehyde and formic acid on TiO_2 were examined by IR spectroscopy [8–16]. According to Busca *et al.* [8], dioxymethylene and polyoxymethylene species are the only products of formaldehyde adsorption on TiO_2 (anatase) at temperatures of –70 to –20°C. At room temperature, these surface species were converted into methoxy groups and formate ions by the Cannizzaro reaction. The formation of dioxymethylene species, formate ions, and methoxy groups in the adsorption of formaldehyde on anatase at room temperature was also observed in [9]. Formaldehyde was oxidized to formate ions on rutile at 100°C [10]. Formates were the major products in formic acid adsorption on both anatase and rutile at 100°C [12–15]. We know of no data on the adsorption of methyl formate on titanium oxide.

In this work, we examined the catalytic properties of TiO_2 (anatase) in the reactions involving formaldehyde and formic acid. The nature of surface intermediates of formaldehyde and products of its selective conversion (formic acid and methyl formate) on TiO_2 (anatase) was studied by *in situ* FTIR spectroscopy.

EXPERIMENTAL

In this study, TiO_2 (anatase) obtained by the spray drying of a hydrogel prepared using a sulfuric acid process [17] was used. The specific surface area of the sample was 100 m^2/g.

The catalytic measurements were performed in a flow-circulation reactor at 110–180°C with the chromatographic analysis of the reaction products. Mixtures with compositions of 2.5% CH_2O in air or helium and 2.5% HCOOH in air or helium were used. The catalytic experiments were performed at a contact time of 1.3 s. The weight of a catalyst sample was 2.9 g.

The *in situ* FTIR studies were performed on a BOMEM MB-102 Fourier transform IR spectrometer in a high-temperature flow IR-cell reactor the design of which has been described elsewhere [18]. A catalyst pellet (1 × 3 cm) weighing ~50 mg was placed in a cell (V = 1.5 cm^3). Before each experiment, the pellet was conditioned in an air flow at 220°C for 1 h immediately in the IR-cell reactor. Then, the cell reactor with the catalyst sample was cooled to 100°C, and the air flow was changed over to a gas flow of the reaction mixture. The gas mixture was supplied at a flow rate of 150 cm^3/min. The following mixtures were used: 2% CH_2O in air (CH_2O/O_2), 2% HCOOH in air ($HCOOH/O_2$), and 2%

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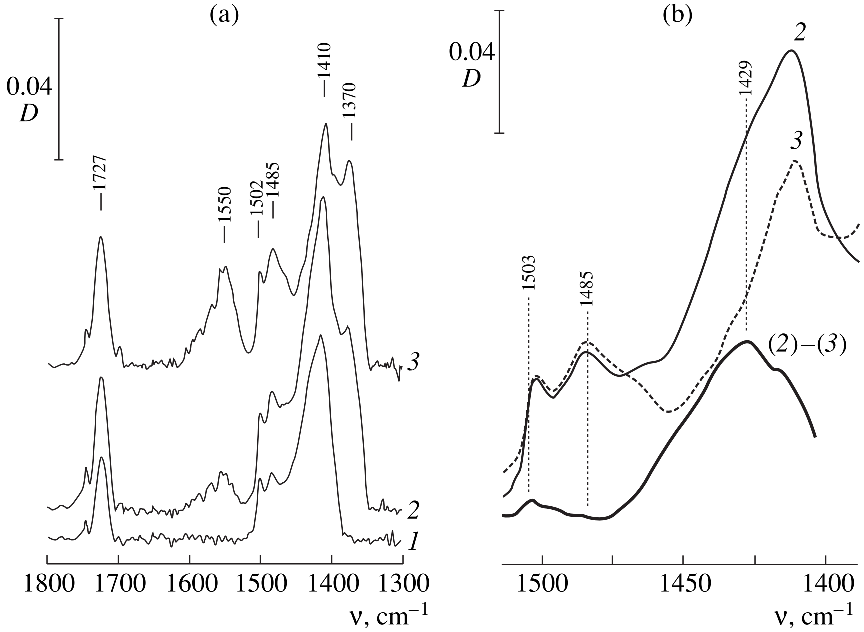


Fig. 1. (a) IR spectra of surface compounds formed under conditions of HCHO adsorption on TiO_2 at 100°C recorded at the adsorption times (*1*) 25, (*2*) 120, and (*3*) 900 s. (b) IR spectrum of TS4 formed by the subtraction of spectrum *3* from spectrum *2* with the subtraction coefficient 1.

$HCOOCH_3$ in air ($HCOOCH_3/O_2$). The CH_2O/O_2 mixture was prepared by the thermal decomposition of paraformaldehyde in an air flow. The $HCOOH/O_2$ and $HCOOCH_3/O_2$ mixtures were prepared by the saturation of air with HCOOH or $HCOOCH_3$ vapor, respectively, at room temperature. All gas lines both upstream and downstream of the cell were kept at a constant temperature to avoid formaldehyde polymerization and condensation of formic acid, methyl formate, and reaction products. The IR spectra were recorded at regular intervals. The time of recording each spectrum was 45 s (10 scans). At the beginning of each experiment, IR spectra were measured in a flow of the reaction mixture at 100°C until steady-state intensities of the absorption bands were attained. Then, the sample was heated to 200°C, and the spectra were recorded at a step of 20 K. The heating rate was 5 K/min. The spectra presented in this paper are superpositions of the spectra of catalysts and adsorbed compounds. To distinguish the spectra of surface compounds, a background spectrum of the catalyst, which was recorded before supplying a reaction mixture to the cell reactor at an appropriate temperature, was subtracted from the initial spectra.

RESULTS

1. Catalytic Properties

Table 1 summarizes the catalytic properties of TiO_2 in the reactions of formaldehyde oxidation and formic acid decomposition. In the temperature range 110–150°C, formaldehyde was converted into methyl formate with high selectivity regardless of the presence of oxygen in the reaction mixture. At higher temperatures, the selectivity to methyl formate decreased; in this case, methanol appeared among the reaction products, and the amount of carbon oxides increased. The activity of TiO_2 in an oxygen-containing mixture was somewhat higher than that in a mixture of formaldehyde with helium.

The decomposition of formic acid on TiO_2 primarily occurred via a dehydration mechanism to form carbon monoxide and water.

2. Adsorption of HCHO

The adsorption of formaldehyde on the surface of TiO_2 at 100°C was accompanied by a decrease in the intensity of the absorption band of adsorbed water δH_2O = 1620 cm^{-1} with a simultaneous increase in the intensities of the absorption bands of adsorbed formaldehyde. This fact indicates that adsorbed H_2O molecules are displaced by HCHO molecules.

Figure 1 shows the IR spectra of surface compounds formed on TiO_2 at different adsorption times when the CH_2O/O_2 reaction mixture was passed through the cell reactor at 100°C. Four groups of absorption bands can be distinguished from the IR spectra of HCHO adsorption products. These groups changed independently of one another as the adsorption time was increased; hence, it follows that they belong to different surface compounds. Three of the four surface compounds detected were identified before in the reactions of HCHO with TiO_2 and other oxides [8–16]. The fre-

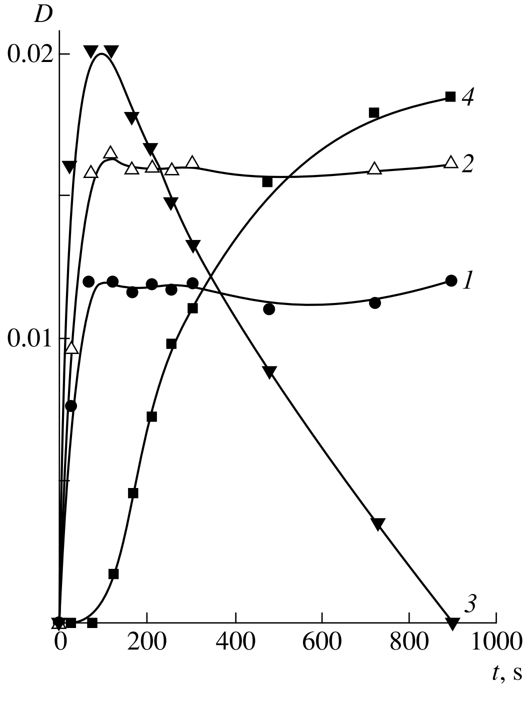


Fig. 2. Intensities of the most typical absorption bands of surface compounds formed under conditions of HCHO adsorption on TiO_2 at 100°C as functions of the adsorption time: (*1*) δCH_2 = 1502 cm^{-1} of H-bonded formaldehyde, (*2*) δCH_2 = 1485 cm^{-1} of dioxymethylene species, (*3*) νCO = 1429 cm^{-1} of bidentate bonded formaldehyde, and (*4*) $\nu_{as}COO$ = 1550 cm^{-1} of bidentate formate.

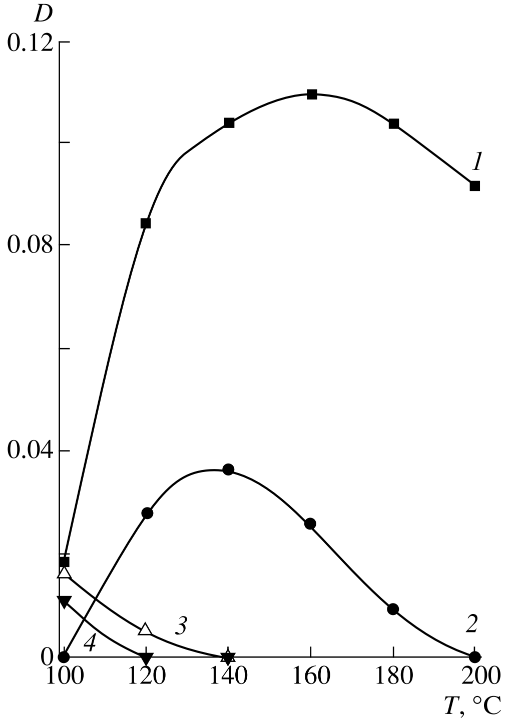


Fig. 3. Intensities of the most typical absorption bands of surface compounds formed under conditions of HCHO adsorption on TiO_2 as functions of temperature: (*1*) $\nu_{as}COO$ = 1550 cm^{-1} of the bidentate formate ion, (*2*) νCO = 1655 cm^{-1} of coordinatively bonded methyl formate, (*3*) δCH_2 = 1485 cm^{-1} of dioxymethylene species, and (*4*) δCH_2 = 1502 cm^{-1} of H-bonded formaldehyde.

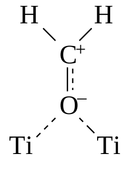
quencies and the assignment of absorption bands are given below.

(1) The absorption bands at 1727 and 1502 cm^{-1} refer to the $\nu C{=}O$ and δCH_2 vibrations of H-bonded formaldehyde (TS1).

(2) The absorption bands at 1485 and 1410 cm^{-1} refer to the δCH_2 and ωCH_2 vibrations of surface dioxymethylene species (TS2).

(3) The absorption bands at 1550 and 1370 cm^{-1} refer to the $\nu_{as}COO$ and ν_sCOO vibrations of bidentate formate ions (TS3).

The fourth surface complex (TS4) was observed only while the catalyst approached a steady state. This complex is characterized by absorption bands at 1429 and 1503 cm^{-1}. Figure 1b demonstrates the spectrum of TS4, which was obtained by the subtraction of the IR spectrum of TiO_2 after formaldehyde adsorption for 120 s (Fig. 1, spectrum *2*) from the corresponding spectrum recorded after passing the CH_2O/O_2 mixture for 900 s (Fig. 1, spectrum *3*). At a subtraction coefficient of 1, the band ωCH_2 = 1410 cm^{-1} for TS2 was fully compensated; this band overlapped with the most intense band of TS4, which has a maximum at 1429 cm^{-1}. The relatively high intensity and half width (≈50 cm^{-1}) of the absorption band at 1429 cm^{-1} as compared with the bands of CH_2 deformation vibrations, which are usually observed in this region of the IR spectra of adsorbed organic compounds, is characteristic of the spectrum of TS4. Taking this fact into account, we believe that the absorption band at 1429 cm^{-1} can be assigned to the νCO vibration in the formaldehyde molecule with bidentate coordination to Ti^{4+} ions (TS4)



TS4

In this mode of coordination, the strong activation of the C=O bond in the formaldehyde molecule results in a considerable decrease in the frequency of the absorption band due to the νCO vibration as compared with νCO in formaldehyde.

Figure 2 demonstrates the intensities of the most typical absorption bands for TS1 (δCH_2 = 1502 cm^{-1}), TS2 (δCH_2 = 1485 cm^{-1}), TS3 ($\nu_{as}COO$ = 1550 cm^{-1}), and TS4 ($\nu C{=}O$ = 1429 cm^{-1}) as functions of adsorp-

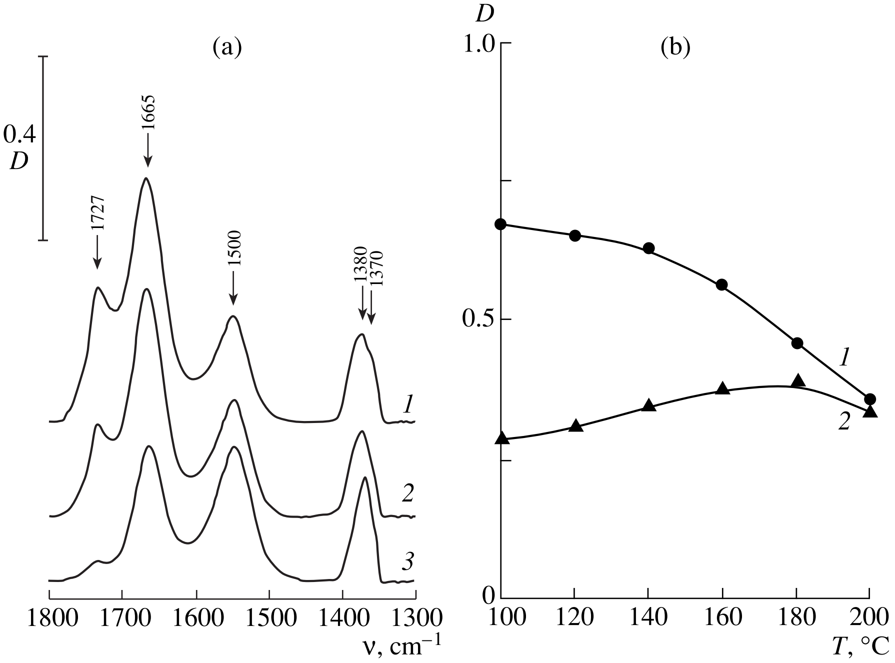


Fig. 4. (a) IR spectra of surface compounds formed under the conditions of HCOOH adsorption on TiO_2 at the temperatures (*1*) 100, (*2*) 140, and (*3*) 200°C. (b) The temperature dependence of the intensities of absorption bands at (*1*) 1665 (due to unsymmetrical formate) and (*2*) 1550 cm^{-1} (due to bidentate formate).

tion time at 100°C. To characterize surface coverage with H-bonded formaldehyde molecules, we chose an absorption band corresponding to the δCH_2 vibration rather than the most intense absorption band $\nu C{=}O$ = 1727 cm^{-1} because the latter strongly overlapped with the absorption band $\nu C{=}O$ of formaldehyde in a gas phase ($\nu C{=}O$ = 1744 cm^{-1}). The coverage of the TiO_2 surface with H-bonded formaldehyde molecules and dioxymethylene complexes attained steady-state values after ~100 s (Fig. 2, curves *1*, *2*). The coverage with coordinatively bonded formaldehyde molecules passed through a maximum at ~100 s (Fig. 2, curve *3*), which coincides in time with the appearance of the absorption bands due to bidentate formate ions in the IR spectrum. The kinetic curve of the formation of bidentate formate ions exhibits an induction period of ~100 s. Then, the surface coverage with these species progressively increased to attain a steady-state value after ~700–900 s (Fig. 2, curve *4*).

Figure 3 shows the temperature dependence of the coverage with surface species (in terms of absorbances at relevant bands) as measured by passing the reaction mixtures through the cell reactor with the catalyst. After attaining the steady-state surface coverage with TS1–TS3 at 100°C, the temperature was increased. In the course of the temperature-programmed reaction, the bands of H-bonded formaldehyde disappeared almost completely at 120°C (Fig. 3, curve *4*). As the temperature increased, the band intensities of dioxymethylene species decreased (Fig. 3, curve *3*) and the absorption bands of the bidentate formate ion increased up to 160°C and then began to decrease (Fig. 3, curve *1*). At ~120°C, a new absorption band at 1655 cm^{-1} appeared in the IR spectra, the intensity of which passed through a maximum at ~140°C (Fig. 3, curve *2*). The frequency of this band is typical of the $\nu C{=}O$ vibrations in surface carbonyl compounds. Taking into account that methyl formate is the major product of formaldehyde conversion on TiO_2 in the temperature range 100–160°C (see the table), we believe that the appearance of this band in the IR spectra is associated with the formation of adsorbed methyl formate. Indeed, as we will discuss below, a similar surface complex, coordinatively bonded methyl formate, was observed in the adsorption of $HCOOCH_3$ on TiO_2 in the same temperature range.

3. *Adsorption of HCOOH*

The adsorption of HCOOH on the surface of TiO_2 at 100°C resulted in the appearance of absorption bands due to a number of surface compounds in the IR spectrum (Fig. 4a, spectrum *1*). Among these bands, the well-known absorption bands of the bidentate formate ion $\nu_{as}COO$ = 1550 cm^{-1} and $\nu_{s}COO$ = 1370 cm^{-1} can be emphasized. The absorption bands at 3185, 2945, 1728, and 1380 cm^{-1} are characteristic of the νOH, νCH, $\nu C{=}O$, and δCH vibrations in the H-bonded formic acid molecule (TS5). The absorption bands at 2946, 2883, and 1665 cm^{-1} are attributed to the νCH and $\nu C{=}O$ vibrations in HCOOH molecules coordinatively bonded to Lewis acid sites (LAS) [19–21]. How-

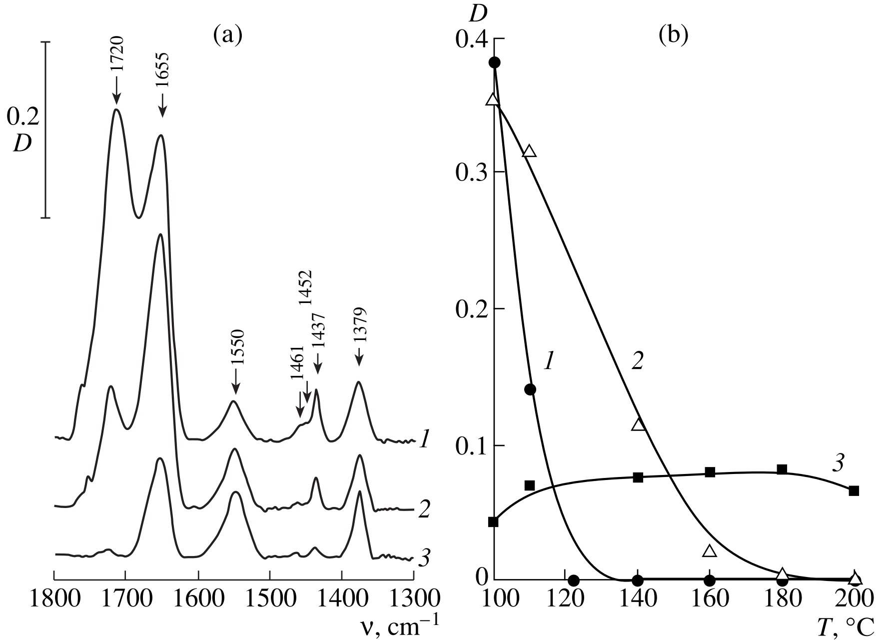
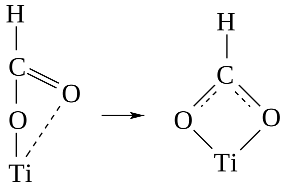


Fig. 5. (a) IR spectra of surface compounds formed under conditions of $HCOOCH_3$ adsorption on TiO_2 at the temperatures (*1*) 110, (*2*) 160, and (*3*) 180°C. (b) The temperature dependence of the intensities of absorption bands at (*1*) 1727 (due to H-bonded methyl formate), (*2*) 1665 (due to coordinatively bonded methyl formate), and (*3*) 1550 cm^{-1} (due to bidentate formate).

ever, in the case under consideration, the absence of an absorption band due to the νOH vibration (3185 cm^{-1}) from the IR spectra of this surface species has attracted our attention. Therefore, we believe that the observed absorption bands at 2946, 2883, and 1665 cm^{-1} also characterize the dissociative adsorption of the acid and can be attributed to the $\nu_{as}COO + \delta CH$, νCH, and νC=O vibrations, respectively, in the formate ion bonded to the surface by a more covalent bond (TS 6) than that in the case of bidentate formate (TS3)



TS6 TS3

The frequency of the absorption band νC=O in this surface compound should be lower than 1300 cm^{-1}, and it cannot be detected in our experiments because of the intense absorption of TiO_2 in this region of the IR spectrum. In a flow of $HCOOH/O_2$ at 100°C, the absorption band intensities of all of the surface compounds increased with time and attained steady-state values after ~800 s. Figure 4b shows the temperature dependence of the intensities of absorption bands of TS3 and TS6. The opposite changes in the surface concentrations for these formates can be indicative of the transformation of the unsymmetrical formate (TS6) to the symmetrical bidentate formate (TS3) with increasing temperature (as shown above).

4. Adsorption of $HCOOCH_3$

Figure 5a demonstrates the IR spectra of the products of $HCOOCH_3$ adsorption on TiO_2. These spectra were recorded on passing the $HCOOCH_3/O_2$ mixture through the cell reactor at 100°C. The absorption bands of several surface species can be recognized in the IR spectrum. In addition to the bands due to the bidentate formate ion ($\nu_{as}COO$ = 1550 cm^{-1} and ν_sCOO = 1379 cm^{-1}) (TS3), the absorption bands of the following two molecularly adsorbed methyl formate species were observed: H-bonded $HCOOCH_3$ (TS7) (the bands at 1727, 1452, and 1437 cm^{-1} ascribed to νC=O, $\delta_{as}CH_3$, and δ_aCH_3, respectively) and methyl formate coordinatively bonded to LAS of TiO_2 (TS8) (the bands at 1655, 1461, and 1437 cm^{-1} ascribed to νC=O, $\delta_{as}CH_3$, and δ_sCH_3, respectively) [12, 22].

Figure 5b demonstrates the temperature dependence of the surface coverage with TS3, TS7, and TS8 complexes. The absorption bands of H-bonded $HCOOCH_3$ disappeared almost completely at 120°C (Fig. 5b, curve *1*). The absorption band intensities of coordinatively bonded $HCOOCH_3$ decreased with temperature (Fig. 5b, curve *2*), and the band intensity of the bidentate formate ion passed through a maximum at 160–180°C (Fig. 5b, curve *3*).

Catalytic properties of TiO_2 in the reactions of formaldehyde oxidation and formic acid decomposition

T, °C	Conversion, %	Selectivity, %				$w \times 10^5$, mol m^{-2} h^{-1}
		$HCOOCH_3$	CO	CO_2	CH_3OH	
2.5% CH_2O in air						
110	30.0	99.1	0.8	0.1	–	1.1
120	36.0	99.0	0.8	0.2	–	1.3
130	44.0	94.5	5.0	0.5	–	1.8
150	52.7	91.7	6.8	1.1	0.4	2.1
180	65.2	75.5	18.2	4.5	1.8	2.7
2.5% CH_2O in helium						
130	40.3	97.3	2.7	–	–	1.3
180	58.5	72.3	20.1	2.3	5.3	1.8
2.5% HCOOH in air						
130	25.5	–	95.2	4.8	–	0.4
180	75.3	–	98.1	1.9	–	2.2

DISCUSSION

Methyl formate is the major product of formaldehyde conversion on TiO_2 (anatase) in the temperature range 110–150°C. The selectivity for this product is >90% in the conversion range 30.0–52.7% (see the table).

The data obtained by *in situ* FTIR spectroscopy suggest that formaldehyde reacts with the TiO_2 surface at 100°C to form H-bonded formaldehyde (TS1), dioxymethylene species (TS2), and coordinatively bonded formaldehyde (TS4). As follows from non-steady-state kinetic curves (Fig. 2), coordinatively bonded formaldehyde is oxidized to bidentate formate (TS3) even at 100°C. As a result, only TS1, TS2, and TS3 can be observed on the surface of TiO_2 in the presence of a reaction mixture under steady-state conditions. Under conditions of the temperature-programmed conversion of formaldehyde, the absorption bands of TS1 can be observed in the IR spectrum only below 110°C. In the temperature range 100–160°C, the concentration of TS2 monotonically decreases. Coordinatively bonded methyl formate (TS8) is formed over the same temperature range, and a maximum selectivity for methyl formate is observed (see the table). These results suggest that dioxymethylene complexes are intermediates in the formation of methyl formate from formaldehyde via TS8. It is well known [9, 12, 16, 22] that methyl formate can be formed by the interaction of formate ions and methoxy groups, and the latter are the metathesis products of dioxymethylene species [8, 9, 11, 22].

As discussed above, coordinatively bonded methyl formate is really the main species in the interaction between methyl formate and the surface of TiO_2. The concentration of this complex dramatically decreases as the temperature increases to 160°C in a flow of either the $HCOOCH_3/O_2$ mixture (Fig. 4) or helium. These data suggest that the complex decomposes with the release of methyl formate to the gas phase. Under the reaction conditions of formaldehyde conversion, the surface concentration of TS8 passes through a maximum at ~150°C.

The selectivity to methyl formate decreases at temperatures higher than 150°C because the amount of carbon oxides in the reaction products increases and methanol is formed (see the table).

It is most likely that the products of complete oxidation are formed by the decomposition of bidentate formates (TS3). Indeed, a decrease in the concentration of bidentate formates (TS3) is observed in the *in situ* FTIR studies in the temperature range above 150°C.

Under the reaction condition of formaldehyde conversion, bidentate formates can be formed via the following three routes:

(1) The oxidation of coordinatively bonded CH_2O (TS4), as follows from non-steady-state experiments (Fig. 2).

(2) The direct oxidation of dioxymethylene complexes (TS2) [8, 9, 11, 22] (this is supported by an increase in the concentration of TS3 as the concentration of TS2 decreases in our experiments under the conditions of a temperature-programmed reaction (Fig. 3)).

(3) The decomposition of methyl formate, a product of formaldehyde conversion. This is supported by direct experiments on the adsorption of methyl formate and formic acid. The spectral characteristics and the thermal stability of bidentate formate formed in the

adsorption of formic acid and methyl formate on TiO_2 (Figs. 4, 5) are identical to the characteristics observed in the adsorption of formaldehyde (Figs. 1, 2).

It is well known [23] that methyl formate is formed with high selectivity in methanol dehydration on some catalysts. It was suggested that formaldehyde is an intermediate in this reaction, and methyl formate is formed by the bimolecular reaction $2HCHO \longrightarrow HCOOCH_3$ [24, 25]. On the basis of the IR-spectroscopic study of methanol conversion on a V_2O_5–TiO_2 catalyst, a mechanism was suggested in [12, 16] for the synthesis of methyl formate via consecutive reactions involving formaldehyde. According to this scheme, methyl formate is formed by the interaction between gaseous methanol and surface formates (the products of formaldehyde adsorption).

On the basis of the results obtained, we believe that the conversion of formaldehyde into methyl formate on TiO_2 occurs via the surface metathesis of dioxymethylene species into methoxy groups and formates followed by the eterification reaction of formates with methoxy groups to form coordinatively bonded methyl formate.

ACKNOWLEDGMENTS

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