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Formaldehyde formation in the interaction of HCOOH with Pt supported on TiO_2

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Abstract

The interaction between HCOOH and TiO_2-supported Pt catalysts was investigated at 300–473 K. The formation of surface species was studied by FTIR and the simultaneous monitoring of the gas phase revealed the formation of the products during the interaction. Besides the dissociative adsorption of HCOOH and the derivatives of this process, the formation of formaldehyde both in the adsorbed layer and in the gas phase was observed. The amount of formaldehyde depended on the pretreatment and on the metal content of the catalysts as well as on the temperature of the interaction. The formaldehyde formation might be an independent reaction pathway in the catalytic transformation of HCOOH.

Keywords: HCOOH adsorption; Formaldehyde formation; FTIR; Mass spectrometry; TiO_2-supported Pt catalysts

1. Introduction

The adsorption and surface reactions of formic acid on TiO_2 and TiO_2-supported metals are important in many respects. Formic acid can easily dissociate producing formate and hydrogen [1,2] on these surfaces. Formate decomposes further to a variety of products, the dominant of which are CO, CO_2, H_2O, and H_2. Taking into account these products, the decomposition of formic acid on TiO_2 surfaces has been described in terms of dehydration (to CO and H_2O) and dehydrogenation (to CO_2 and H_2) mechanisms [3–8]. It was proposed that the dehydration is a unimolecular process (favorable at temperatures above 500 K), while the dehydrogenation is a bimolecular reaction (favorable at temperatures below 500 K) involving HCOOH from the gas phase [5]. It was found, however, that these findings seem to depend very sensitively on the reaction conditions. It was demonstrated that water and CO desorptions are not directly linked; therefore, a simple unimolecular reaction could be excluded. It was also stated that oxygen vacancies should play a decisive role in the decomposition process. In the presence of metal on TiO_2 surface (Pd on $TiO_2(110)$) [9] CO species bound to Pd were detected besides surface formate. The interaction of formate with oxygen vacancies leads to the formation of formaldehyde [10,11]. Two routes of formaldehyde formation were proposed: the first, on reduced surfaces, involves the reduction of formic acid to formaldehyde accompanied by the oxidation of surface Ti cations, while a second route for formaldehyde formation, operative on fully oxidized surfaces, involves bimolecular coupling of two formates [11].

The above conclusions have been made mostly for well-defined TiO_2 single crystal surfaces. Interestingly, we have not found such detailed studies and conclusions on powdered TiO_2 samples.

In the present work an attempt was made to study formic acid adsorption on differently pretreated powdered samples. The formation of surface species was monitored by FTIR spectroscopy and the changes in the gas phase were registered by mass spectroscopy. Based on the data obtained, special attention has been paid to the possible link between the dehydration/dehydrogenation processes and the formation of formaldehyde.

2. Experimental

TiO_2 was the product of Degussa (P25, 50 m^2/g). 1 and **w** 5% Pt/TiO_2 catalyst were prepared by impregnating of

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TiO_2 with an aqueous solution of $H_2PtCl_6 \cdot 3H_2O$ salt (Reanal). The impregnated powders were dried at 383 K for 3 h. Formic acid was of 99.9% purity (Merck) and it was used after a freeze and pump purification process.

For IR studies the catalysts' powders were pressed onto a Ta-mesh (30×10 mm, 5 mg/cm^2). The mesh was fixed to the bottom of a conventional UHV sample manipulator. It was resistively heated and the temperature of the sample was measured by NiCr–Ni thermocouple spot-welded directly to the mesh. The pretreatments of the samples were performed in a stainless-steel UV IR cell (base pressure 10^{-7} Torr): TiO_2 samples were (a) evacuated at 473, 573, and 673 K for 1 h; (b) heated in 1 Torr of O_2 (133.3 Pa) up to 573 K and kept at this temperature for 1 h; or (c) heated in 1 Torr of H_2 (133.3 Pa) up to 573 K and kept at this temperature for 1 h. The b and c steps were followed by degassing at the same temperature for 30 min and by cooling the sample to the temperature of the experiment. The 1 and 5% Pt/TiO_2 samples were pretreated according to b and c. Infrared spectra were recorded with a Genesis (Mattson) FTIR spectrometer with a wavenumber accuracy of ±4 cm^{-1}. Typically 136 scans were collected. The whole optical path was purged with CO_2- and H_2O-free air generated by a Balston 75-62 FTIR purge gas generator. The spectrum of the pretreated sample (background spectrum) and the actual vapor spectrum were subtracted from the spectrum registered in the presence of vapor. The spectra presented here are the results of this doubled subtraction. All subtractions were taken without use of a scaling factor ($f = 1.000$). Mass spectrometric analysis was performed with the help of a QMS 200 (Balzers) quadrupole mass spectrometer. The volume around the head of QMS 200 was continuously evacuated and it was connected with the UV IR cell via a leak valve producing 5×10^{-6} Torr around the MS head when reacting gases were present in the cell. The changes in the signal intensity of the main fragments of formic acid and the possible products were followed by mass spectrometry. With the help of a homemade algorithm one can calculate the intensity characterizing only the given product (generally the most intense fragment signal of a molecule) by taking into account the contributions of any other fragments to this signal. The contributions were calculated on the basis of intensity ratios between the fragments characteristic of the individual molecules. The intensity ratios measured in our system during MS analyses of the starting materials and the possible products did not differ considerably from the intensity ratios published in the literature.

The dispersity of the reduced sample was 29% for 1% Pt/TiO_2 and 27% for 5% Pt/TiO_2 determined by H_2 adsorption at room temperature. The average particle size calculated from the dispersity data [12,13] was 3.1 nm for 1% Pt/TiO_2 and 3.3 nm for 5% Pt/TiO_2.

3. Results

3.1. Infrared studies

3.1.1. IR spectra registered in HCOOH adsorption

The adsorption of HCOOH (1 Torr) at 300 K for 1 h on TiO_2 evacuated at different temperatures caused the appearance of the bands at 2959, 2924, 2867, 2734, 1712 (sh), 1673, 1573, 1370, 1318 (sh), 1270 (sh), 1166, and 1068 cm^{-1} (Fig. 1). Note, that these spectra are due to the adsorbed layer formed on the surface of catalysts, as they are

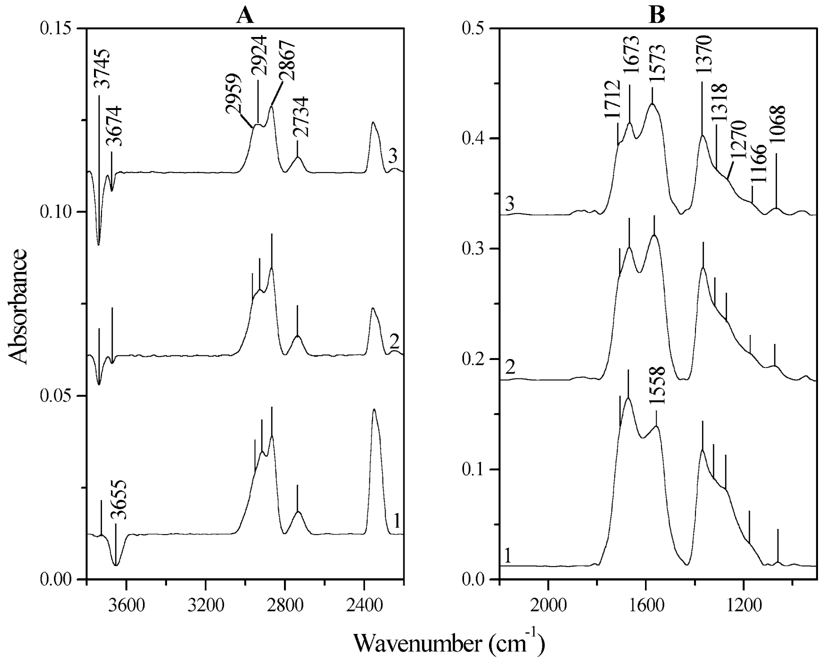

Fig. 1. IR spectra recorded in the adsorption of HCOOH (1 Torr) at 300 K for 1 h on differently pretreated TiO_2: (1) TiO_2 evacuated at 473 K for 1 h; (2) TiO_2 evacuated at 573 K for 1 h; and (3) TiO_2 evacuated at 673 K for 1 h.

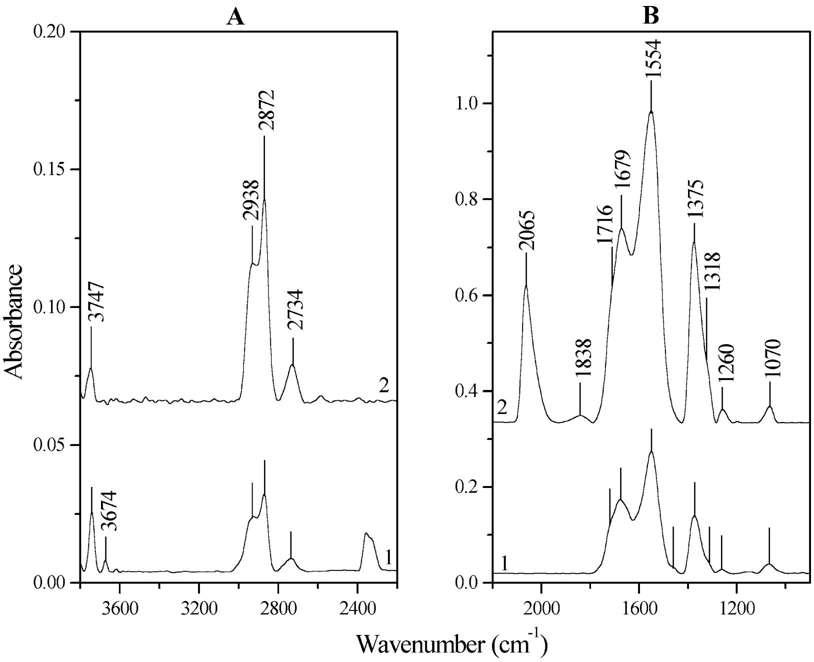

Fig. 2. IR spectra recorded in the adsorption of HCOOH (1 Torr) at 300 K for 1 h on reduced catalysts: (1) TiO_2 and (2) 5% Pt/TiO_2.

the results of the subtractions of background spectrum and the gas phase spectrum from the spectrum taken in HCOOH. The intensities of these bands slightly decreased with the increase of the evacuation temperature. The formation of adsorbed CO_2 (band at 2360–2330 cm^{-1}) was also detected. The negative features at 3745 and 3674 (3655) cm^{-1} should be connected with the consumption of the surface OH groups during the interaction of HCOOH with the surface. It is noteworthy that the intensity of the negative feature at 3745 cm^{-1} increases with the increase of the evacuation temperature, which means that the consumption of the surface OH groups occurred in the highest extent on TiO_2 previously evacuated at 673 K. It has to be noted that bands in the range of 1800–2200 cm^{-1} were not observed on TiO_2 samples.

HCOOH adsorption at 300 K on reduced catalysts resulted in slightly different spectra (Fig. 2A, spectrum 1). Instead of OH groups' consumption observed on TiO_2 samples evacuated at different temperatures, the formation of new OH groups (3747 and 3674 cm^{-1}) was registered in HCOOH adsorption on reduced catalysts. Interestingly only one band at 2938 cm^{-1} appeared on the reduced samples in contrast with the 2959 and 2924 cm^{-1} bands observed on TiO_2 evacuated at different temperatures. The other bands (2872, 2734, 1716 (sh), 1679, 1554, 1375, 1318 (sh), 1260, and 1070 cm^{-1}) were registered at nearly the same wavenumbers, as on evacuated TiO_2 surfaces. The presence of Pt adatoms changes the IR features (Fig. 2B, spectrum 2). Due to the presence of Pt, bands assigned to CO linearly adsorbed on Pt (2065 cm^{-1}) and to CO bridge-bonded to two Pt atoms (1838 cm^{-1}) were observed on 1 and 5% Pt/TiO_2 catalysts reduced at 573 K.

Some spectra registered in the presence of HCOOH at different temperatures are shown in Fig. 3 for reduced TiO_2 (A) and for reduced 5% Pt/TiO_2 (B). The obvious difference is the detection of the bands due to adsorbed CO (2065 and 1838 cm^{-1}) on Pt-containing catalysts at 300–473 K. On pure TiO_2 no bands in the range of 1800–2200 cm^{-1} were observed at any temperatures. Although their intensities decreased, the bands at 1716 and 1679 cm^{-1} could be observed even at 383 K on TiO_2. On the spectrum of 5% Pt/TiO_2 registered at 383 K, however, these bands were missing. At 473 K the bands at 1554 and 1375 cm^{-1} were detected on the spectrum of TiO_2, on the spectrum of 5% Pt/TiO_2; however, only the 2065 cm^{-1} band was clearly observed.

3.1.2. Infrared evidence for surface formaldehyde

The adsorption experiments were finished by evacuation at the adsorption temperatures, and spectra due to the surface species stable against evacuation were registered at the given temperature. When the spectra taken after evacuation were subtracted from the spectra due to adsorbed layer, a positive band at 1712–1716 cm^{-1} was detected. For the better understanding of this process, an example is given on Fig. 4. The positive band at 1712–1716 cm^{-1} might be assigned to surface formaldehyde ($CH_2O_{(a)}$) formed during the HCOOH adsorption. These surface species are stable only in the presence of HCOOH vapor, as evacuation at any temperatures eliminated the band due to this surface species.

The integrated absorbance values of the (positive) 1712–1716 cm^{-1} band were plotted for oxidized (Fig. 5A) and reduced (Fig. 5B) catalysts. The surface concentration of adsorbed formaldehyde seems to be dependent on the pretreatment, on the Pt content and on the adsorption temperature.

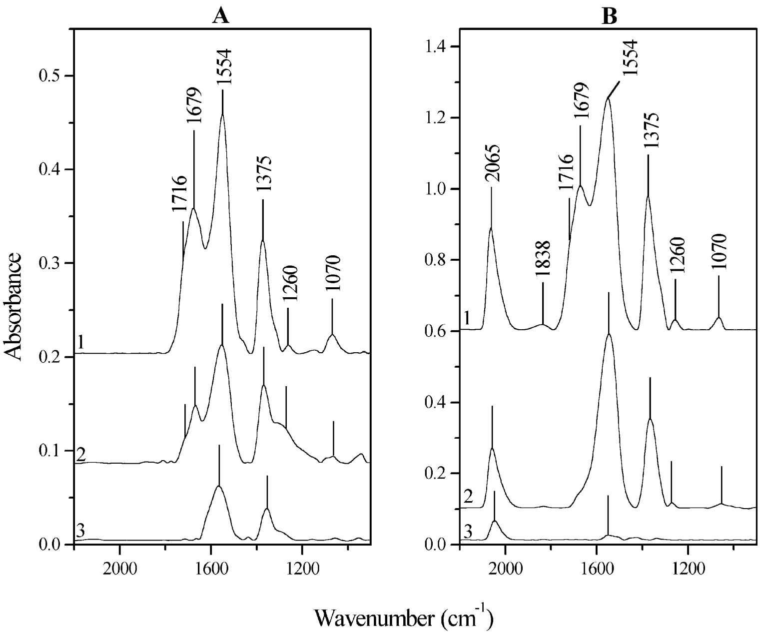

Fig. 3. IR spectra recorded in the adsorption of HCOOH (1 Torr) at different temperatures for 1 h on reduced TiO_2 (A) and 5% Pt/TiO_2 (B): (1) 300 K; (2) 383 K; and (3) 473 K. (The spectra were registered at the temperatures of adsorption.)

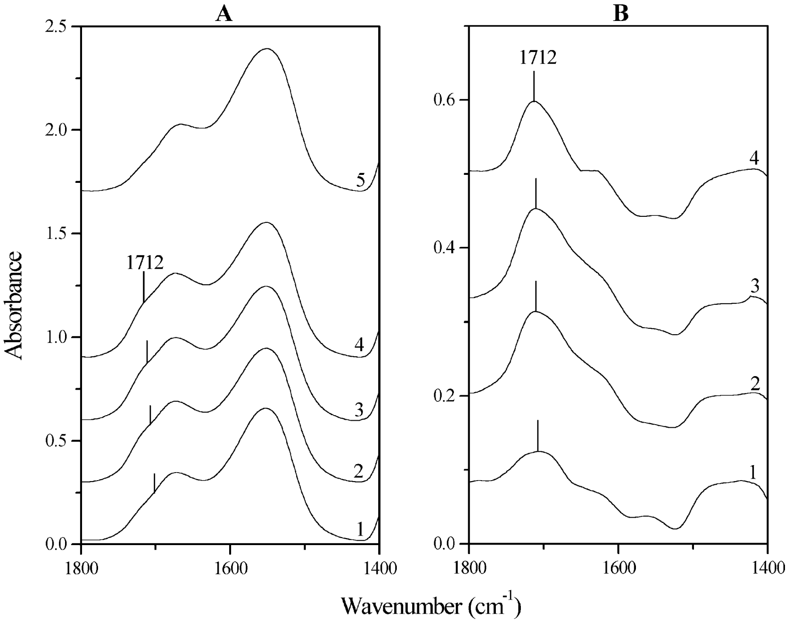

Fig. 4. (A) IR spectra of HCOOH (1 Torr) adsorption at 300 K on reduced 5% Pt/TiO_2: (1) 1 min; (2) 15 min; (3) 30 min; (4) 60 min; and (5) subsequent evacuation at 300 K for 15 min. (B) Difference spectra obtained by subtraction of spectrum 5 in Fig. 4A from: (1) spectrum 1; (2) spectrum 2; (3) spectrum 3; and (4) spectrum 4 of Fig. 4A.

The integrated absorbance values were higher on oxidized surfaces. The highest integrated absorbance values were observed on 5% Pt/TiO_2 at 300 K. The band due to $CH_2O_{(a)}$ could be detected with relatively high integrated absorbance values on TiO_2 at 383 K, but in the presence of Pt the surface concentration of $CH_2O_{(a)}$ greatly reduced (1% Pt/TiO_2), or it completely disappeared (5% Pt/TiO_2) at this temperature. The increase of the adsorption temperature to 473 K caused a marked decrease of the $CH_2O_{(a)}$ surface concentration even on TiO_2.

3.2. Mass spectroscopic measurements

Besides the products of dehydration (CO and H_2O) and dehydrogenation (CO_2 and H_2), formaldehyde, methane and ethylene were detected in the gas phase during HCOOH adsorption at 300–473 K. Their appearance and amounts depended on the pretreatment and on the metal content of the catalysts and on the temperature.

In the adsorption of HCOOH at 300 K on oxidized surfaces there were no great differences in the amounts of

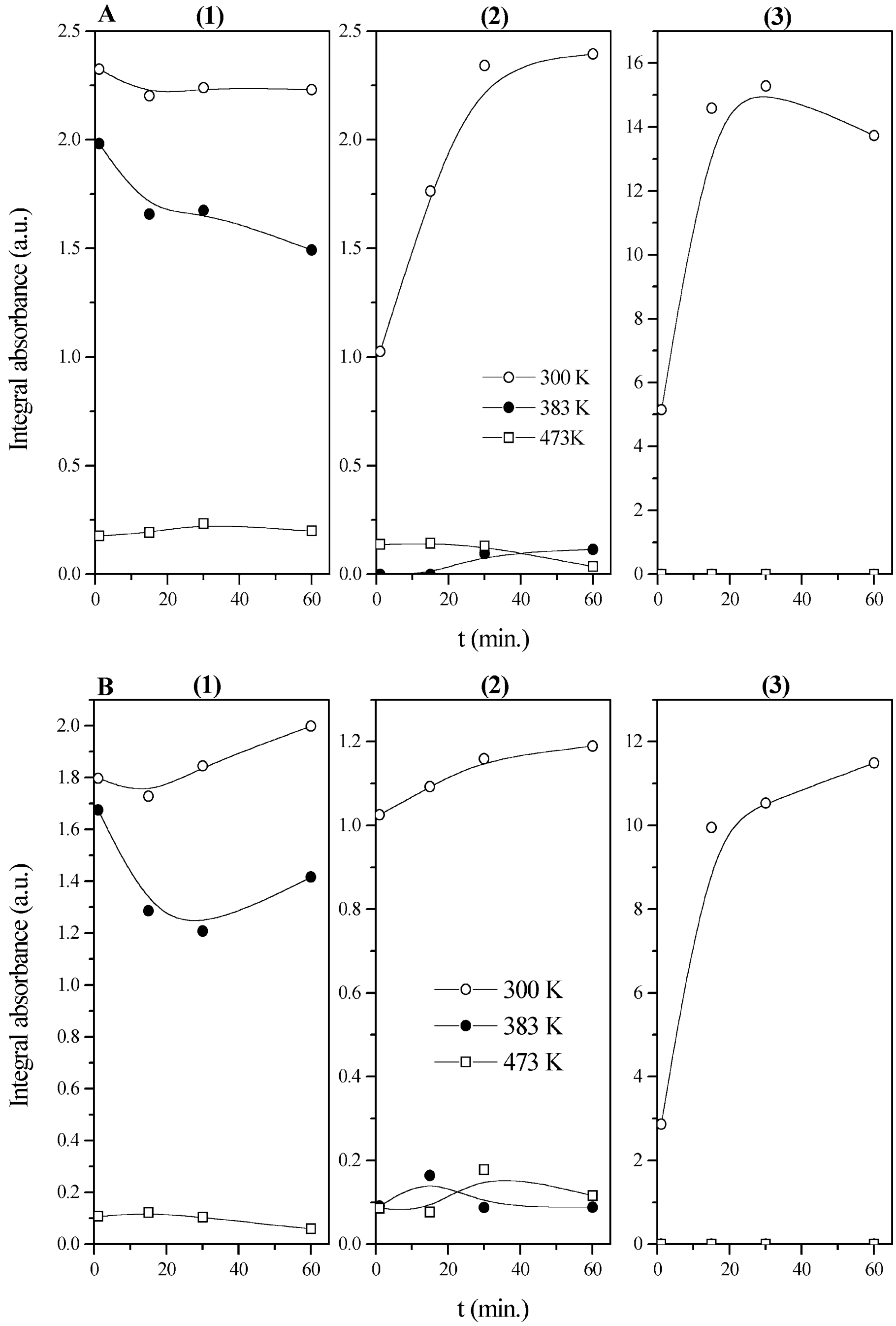

Fig. 5. Integral absorbances of the band due to formaldehyde in the adsorbed layer (see text) measured at different temperatures on: (A) oxidized catalysts and (B) reduced catalysts; (1) TiO_2; (2) 1% Pt/TiO_2; and (3) 5% Pt/TiO_2.

formic acid, formaldehyde, CO_2, H_2, H_2O, and CH_4. CO did not appear in the gas phase in the interaction between HCOOH and oxidized TiO_2 and Pt-containing TiO_2 catalysts at 300 K. The amount of ethylene was the highest on TiO_2 and decreased with the increase of Pt content of the catalysts. At 383 K (Fig. 6) the amount of H_2 and CO_2 slightly increased on 5% Pt/TiO_2 catalyst in comparison with that observed on TiO_2. It is important to note that on 5% Pt/TiO_2 catalyst CO appeared in the gas phase. No CO formation in the interaction of HCOOH with oxidized TiO_2 was observed at 383 K. The amount of gas-phase formaldehyde formed in the interaction at 383 K decreased with the increase of Pt content of the catalysts. The consumption of formic acid was four times higher on the Pt-containing catalysts than on TiO_2. At 473 K the results were similar to those observed at 383 K with the exception that CO appeared in the gas phase even on TiO_2.

The reduction of the catalysts did not influence basically the gas-phase changes observed on oxidized surfaces during HCOOH adsorption at 300–473 K.

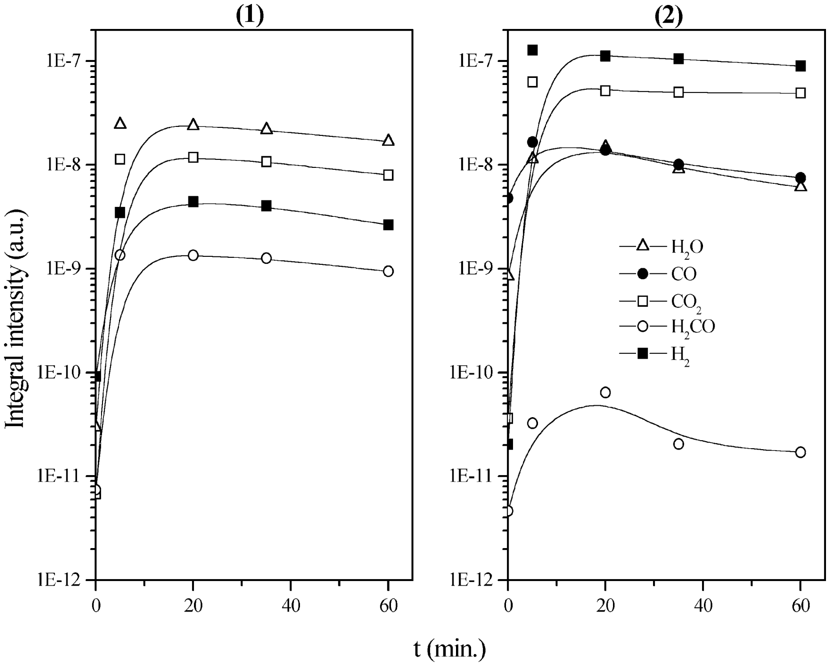

Fig. 6. Mass spectrometric analysis of the gas phase during the interaction between HCOOH (1 Torr) and oxidized catalysts at 383 K: (1) TiO_2 and (2) 5% Pt/TiO_2.

Table 1
Vibrational frequencies (in cm^{-1}) of HCOOH gas and molecularly adsorbed HCOOH

Assignment	HCOOH gas [14]	$HCOOH_{(a)}$ on TiO_2 powder [15]	$HCOOH_{(a)}$ on TiO_2 powder [16]	$HCOOH_{(a)}$ on TiO_2 (110)[a] [10,17]
OH stretch	3750			
CH stretch	2943			2950, 2970
C=O stretch	1770	1670	1682	1670, 1690
CH bend	1387	1332	1325	1405, 1390
OH bend	1229			1235
CO stretch	1105	1278	1277	
CH bend	1033			
OCO deform	625			

[a] Various modes of multilayer formic acid.

Table 2
Vibrational frequencies (in cm^{-1}) characteristic of adsorbed formate species ($HCOO_{(a)}$) formed in HCOOH adsorption

Assignment	TiO_2 (powder) [15]	TiO_2 (powder) [16]	TiO_2 (110) [9]	TiO_2 (110) [10]
Combination of	2977		2928	2920
ν_a(OCO) and CH def.	2952			
ν(CH)	2872			
$\nu_a(OCO) + \delta_a(CH)$	2754			
ν_a(OCO)	1552	1560	1524	
	1537	1553		
δ(CH) or	1413	1410	1379	1365
γ(OCO)	1386	1381		
		1379		
ν_s(OCO)	1370	1356		
	1359			

Table 3
Characteristic bands (in cm^{-1}) of gaseous formaldehyde [14]

Assignment	H_2CO gas
CH_2 asym. str.	2843
CH_2 sym. str.	2783
CO stretch	1746
CH_2 scissor	1500
CH_2 rocking	1249
CH_2 wagging	1167

4. Discussion

Based on literature assignments (Tables 1–3), the assignments of the bands that are characteristic of the adsorbed layer formed during HCOOH adsorption and presented in this work on different catalysts are collected in Table 4.

According to these assignments and to the former literature conclusions, HCOOH can easily dissociate to form $HCOO_{(a)}$ on the surfaces investigated. The important finding of our study was the detection of formaldehyde in the adsorbed layer. Besides these adsorbed species, molecularly adsorbed HCOOH and (on Pt-containing catalysts) CO adsorbed on the metal component were also detected.

The dissociation of HCOOH on TiO_2 evacuated at different temperatures and on oxidized surfaces led to the consumption of surface OH groups, which can be explained by

$$HCOOH_{(g)} + OH_{(s)} \rightarrow HCOO_{(a)} + H_2O \quad (1)$$

surface reaction. One of the OH groups (band at 3745 cm^{-1}) participating in this process is due to the small amount of

Table 4
Bands (in cm^{-1}) observed in HCOOH adsorption and their assignments[a]

Assignment	TiO_2	1% Pt/TiO_2	5% Pt/TiO_2
$\nu_a(OCO) + \delta(CH)$ in $HCOO_{(a)}$	2959	2952	–
$\nu(CH)$ in $HCOOH_{(a)}$	2938	2938	2938
$\nu(CH)$ in $HCOO_{(a)}$	2872	2872	2872
$\nu_s(OCO) + \delta(CH)$ in $HCOO_{(a)}$	2734	2734	2734
$\nu(CO)$ in $Pt–CO_{(a)}$		2057–2065	2057–2065
$\nu(CO)$ in $(Pt)_2–CO_{(a)}$		1838	1838
$\nu(CO)$ in $H_2CO_{(a)}$	1712	1716	1716
$\nu(CO)$ in $HCOOH_{(a)}$	1673	1679	1679
$\delta(H_2O)$	1650	1646	
$\nu_a(OCO)$ in $HCOO_{(a)}$	1573	1554	1554
$\omega(CH_2)$ in $H_2CO_{(a)}$		1509	
$\nu_s(OCO)$ in $HCOO_{(a)}$	1370	1375	1376
$\gamma(CH_2)$ in $H_2CO_{(a)}$	1270	1260	1260
$\tau(CH_2)$ in $H_2CO_{(a)}$	1166	1166	

[a] This work.

silica impurity [18]. The other OH group (band at 3674–3655 cm^{-1}) can be connected with the surface OH of anatase [19]. Water formed in reaction (1) may remain on the surface, or it may desorb into the gas phase.

On reduced surfaces the surface concentration of OH groups increased due to HCOOH adsorption:

$$HCOOH_{(g)} + O_{(s)} \rightarrow HCOO_{(a)} + OH_{(a)}. \quad (2)$$

The appearance of different OH bands during this process may be due to the formation of OH groups on different surface oxygen coordinated by different number of metal (Ti^{+4}) sites [19]. The formation of $HCOO_{(a)}$ surface species depended on the metal content and on the adsorption temperature. Interestingly, at 300 K with the increase of the Pt content of the catalysts the intensities of the bands due to $HCOO_{(a)}$ increased; i.e., the surface concentration of these surface species was greater on 5% Pt/TiO_2 catalysts than on TiO_2 itself. It could be assumed that HCOOH dissociation is presumably more facile and occurred in a greater extent on Pt sites as on the surface sites ($OH_{(s)}$ and $O_{(a)}$) of TiO_2. HCOO species formed in the dissociation of HCOOH on Pt sites migrate from the metal to the support and localize there [20].

A part of HCOOH can directly decompose on Pt sites:

$$HCOOH_{(a)} + Pt_{(s)} \rightarrow Pt–CO + H_2O \quad (3)$$

(Pt–CO denotes here both Pt–CO and $(Pt)_2$–CO surface species). This reaction would cause the appearance of the bands due to CO adsorbed on Pt at 300 K (Figs. 2 and 3B).

Molecularly adsorbed HCOOH and $HCOO_{(a)}$ species were more stable on TiO_2 than on Pt-containing catalysts at elevated temperatures: the bands due to molecularly adsorbed HCOOH (1679 cm^{-1}) and due to $HCOO_{(a)}$ (1554 and 1375 cm^{-1}) appeared with measurable intensities on the spectrum of TiO_2 even at 383 K. At this temperature the band due to molecularly adsorbed HCOOH (1679 cm^{-1}) was missing on the spectrum of 5% Pt/TiO_2. The bands assigned to $HCOO_{(a)}$ were observed on the spectrum of TiO_2 even at 473 K, on the spectrum of 5% Pt/TiO_2; however, these bands disappeared at this temperature (Fig. 3). These observations can be connected with the reactivity of Pt in the decomposition and/or transformation of $HCOOH_{(a)}$ and $HCOO_{(a)}$, respectively.

It has been previously stated [10,11] that the formation of formaldehyde is a result of the interaction of formate with the oxygen vacancies of TiO_2. We observed the formation of formaldehyde in the adsorbed layer on TiO_2, but a direct correlation between the surface concentration of oxygen vacancies (produced by different pretreatments of TiO_2) and the extent of formaldehyde formation could not be established. We found that the extent of the formaldehyde formation in the adsorbed layer was enhanced by the presence of Pt.

We suppose that oxygen vacancies on the TiO_2 surface and/or the metal sites may act as surface centers for deoxygenation of HCOOH:

$$HCOOH + Ti^{3+}–\square \rightarrow CH_2O_{(a)} + Ti^{4+}–O \quad (4)$$

(where $\square$ denotes oxygen vacancy) and/or

$$HCOOH_{(a)} + Pt_{(s)} \rightarrow CH_2O_{(a)} + Pt–O. \quad (5)$$

Our data strengthen the former conclusion [9] that water and CO desorption cannot be directly linked; therefore, a simple unimolecular reaction of formate (dehydration mechanism) could be excluded. Water was detected in the gas phase during the HCOOH adsorption at 300 K on all catalysts investigated, but no CO formation was observed. CO appeared in the gas phase first in HCOOH adsorption on Pt-containing catalysts at 383 K.

Very interesting correlation can be drawn between CO formation and formaldehyde production on Pt-containing catalysts: at 300 K formaldehyde was detected both in the adsorbed layer and in the gas phase, no CO was found in the gas phase. With the increase of the adsorption temperature to 383 K, the surface concentration of $CH_2O_{(a)}$ and the amount of formaldehyde in the gas phase continuously decreased, while CO appeared among the gas phase products. These findings suggest that at 383–473 K the main source of gas phase CO during HCOOH interaction with the Pt/TiO_2 samples would be the decomposition of formaldehyde:

$$CH_2O_{(a)} \rightarrow CO_{(g)} + H_{2(g)}. \quad (6)$$

Another interesting result was the detection of ethylene in the gas phase. Its amount decreased with the increase of Pt content of the catalysts and that of adsorption temperature. Our results revealed that surface sites active in these surface events are in the highest surface concentration on TiO_2, as the highest amount of ethylene was observed on TiO_2 in the adsorption of HCOOH at 300 K. The amounts of formaldehyde and ethylene changed complementary in our experiments. In order to clarify the formation of C_2H_4 we investigated the reaction of formaldehyde to ethylene on the same catalysts in separate experiments [21]. Shortly, we came to the conclusion that the formation of ethylene possibly needs the production of $CH_{2(a)}$ surface species and their coupling. We note here that reductive coupling of carbonyls on TiO_2 was experienced earlier [22]. Ethylene was also detected from formic acid on reduced $UO_2(111)$ single crystal surfaces [23,24].

5. Conclusions

1. The formation of formaldehyde both in the adsorbed layer and in the gas phase was detected on the catalysts investigated.
2. The amount of formaldehyde depended on the pretreatment, the metal content of the catalysts and on the temperature of the interaction.
3. Formaldehyde formation may occur through deoxygenation of formic acid on the oxygen vacancies of titania surface and/or on the metal sites.
4. The main source of gas phase CO is the decomposition of formaldehyde.

Acknowledgments

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