

FTIR and mass spectrometric study of HCOOH interaction with TiO₂ supported Rh and Au catalysts

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Abstract

The decomposition of formic acid on Rh/TiO₂ and Au/TiO₂ catalysts was examined at 300–473 K with Fourier transform infrared spectroscopy (FTIR) and mass spectrometry (MS). Besides molecularly adsorbed HCOOH and formate species (produced in the HCOOH dissociation on the surfaces), formation of formaldehyde was detected by FTIR in the adsorbed layer. The surface concentration of formaldehyde depended on the nature of the metal, as well as on the reaction temperature. A part of formaldehyde desorbed from the adsorbed layer, another part, however, decomposed into H₂ and CO. It is suggested that CO is not the product of the direct dehydration of HCOOH. CO is rather produced in the decomposition of formaldehyde originating from the deoxygenation of HCOOH.

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1. Introduction

The catalytic decomposition of formic acid on TiO₂ single crystal surfaces has been described in terms of dehydration (to CO and H₂O) and dehydrogenation (to CO₂ and H₂) mechanisms [1–6]. It was proposed that CO and H₂O formed in a unimolecular process, while CO₂ and H₂ are the products of a bimolecular reaction involving HCOOH from the gas phase [5]. As water and CO desorption proved to be not directly linked, the simple unimolecular reaction could be excluded [7]. During the interaction between HCOOH and the single crystal surfaces of TiO₂ the formation of gas phase formaldehyde was also observed [7,8]. Two routes of formaldehyde formation were proposed: (i) on reduced surfaces the reduction of formic acid to formaldehyde caused the oxidation of surface Ti cations and (ii) on fully oxidized surfaces two formate species (originating from the dissociative adsorption of HCOOH) react in a bimolecular coupling reaction [8].

On the TiO₂(110)-(1 × 1) surface only the dehydration reaction (above 500 K) has been observed, there was no evidence for dehydrogenation; when the surface was loaded

with Pd nanoparticles, however, then the dehydrogenation reaction (beginning at about 350 K) was also detected [9,21].

Recently we have found [10] that during the interaction of HCOOH with powdered TiO₂ and Pt/TiO₂ catalysts formaldehyde can be detected both in the adsorbed layer and in the gas phase. The extent of formaldehyde formation was higher at low reaction temperature and in the presence of Pt. It has been proposed that the decomposition of formaldehyde at higher temperatures is the main source of CO formation.

As a continuation of our previous studies in this work the reaction of HCOOH on powdered Rh/TiO₂ and Au/TiO₂ catalysts has been studied by FTIR and mass spectrometry. Our primary aim was to collect data on the effect of different metals on the above processes.

2. Experimental

TiO₂ was the product of Degussa (P25, 50 m²/g). One and five percent Rh/TiO₂ catalysts were prepared by impregnating of TiO₂ with an aqueous solution of RhCl₃ × 3H₂O (Johnson Matthey). The impregnated powders were dried at 383 K for 3 h. TiO₂ supported Au catalysts (1 and 5%) were made by a deposition–precipitation method. Chloroauric acid (HAuCl₄·aq p.a. 49% Au, Fluka AG) was first dissolved

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in triply distilled water. After the pH of the HAuCl_4 aqueous solution was adjusted to 7.5 pH adding 1 M NaOH solution, the fine powder of oxidic support was suspended and kept at 343 K for 1 h with continuous stirring. The suspension was aged for 24 h at room temperature and washed with distilled water repeatedly, dried at 353 K and then calcined in air at 573 K for 4 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 mm \times 10 mm, 5 mg/cm²). 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): (a) heated in 1 Torr of O_2 (133.3 Pa) up to 573 K and it was kept at this temperature for 1 h; or (b) heated in 1 Torr of H_2 (133.3 Pa) up to 573 K and it was kept at this temperature for 1 h. The (a) and (b) steps were followed by degassing at the same temperature for 30 min and by cooling the sample to the temperature of the experiment. The dispersion of Rh were determined via H_2 adsorption at 298 K with the use of a dynamic impulse method [11]: the dispersion of reduced 1% Rh/TiO₂ was 30% [12] and that of 5% Rh/TiO₂ was 27%. The dispersion of Au was measured by CO adsorption following the method suggested by Shastri et al. [13]. Whereas the dispersion of Au was relatively high (46%) for 1% Au/TiO₂, this value decreased to 7% for 5% Au/TiO₂ [14]. The average particle sizes were calculated on the basis of dispersity data [15,16]: the average particle size of Rh was 2.88 nm on 1% Rh/TiO₂, 3.2 nm on 5% Rh/TiO₂, and that of Au was 1.96 nm on 1% Au/TiO₂ and 12.9 nm on 5% Au/TiO₂.

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 by CO₂- and H₂O-free air generated by a Balston 75–62 FT-IR purge gas generator. The spectrum of the pretreated sample (background spectrum) and the actual vapour spectrum were subtracted from the spectrum registered in the presence of vapour. 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 spectrometer. With the help of a home made 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 the intensity ratios of the fragments characteristics 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.

3. Results

First HCOOH of different pressures (0.01–1 Torr) was introduced at 300 K onto the reduced 1% Rh/TiO₂ (Fig. 1A) and 1% Au/TiO₂ (Fig. 1B), respectively. The bands appeared at the lowest HCOOH pressure after 5 min adsorption show the presence of molecularly adsorbed HCOOH (2928, 1671 and 1658 cm⁻¹) and that of formate species (2962–2955 cm⁻¹, 2872–2868 cm⁻¹, 2734–2764 cm⁻¹, 1556–1550 cm⁻¹ and 1374–1367 cm⁻¹) formed in the dissociative adsorption of HCOOH. Bands due to formaldehyde in the adsorbed layer (1712, 1272 and 1166 cm⁻¹ for 1% Rh/TiO₂, and 1278 cm⁻¹ for 1% Au/TiO₂) were also detected. With the increase of HCOOH pressure the intensities of the bands listed above increased. In 0.1 and 1 Torr HCOOH the 1708 cm⁻¹ band (due to CH₂O_(a)) was distinguished also on the spectra of 1% Au/TiO₂ (Fig. 1B). Bands due to adsorbed CO species (2149, 2030, 1910 and 1862 cm⁻¹) were detected on the spectra of 1% Rh/TiO₂ taken at 300 K after 5 min adsorption (Fig. 1A). No such kind of spectral features in the CO regime were detected on the gold containing surface at this exposure. A small band due to adsorbed CO (2032 cm⁻¹) appeared only after 60 min adsorption of 1 Torr HCOOH at 300 K in the case of 1% Au/TiO₂ (Fig. 2B).

The same spectral features were registered on oxidized 1% metal/TiO₂ catalysts and on 5% metal/TiO₂ (oxidized and reduced) samples. Interestingly, the intensities of the bands were higher on the oxidized catalysts and smaller on the samples with higher metal loading.

In the next experiments HCOOH (1 Torr) was added to the catalysts at different temperatures and the spectra were registered at the adsorption temperature. Spectra taken at different temperatures after 60 min adsorption time are shown in Fig. 2A (1% Rh/TiO₂) and Fig. 2B (1% Au/TiO₂). Above 1800 cm⁻¹ bands due to adsorbed CO species appeared at all temperatures in the spectra of 1% Rh/TiO₂; CO band of very low intensity was observed only at 300 K on 1% Au/TiO₂. Another difference between the two catalysts is demonstrated by the stability of the bands due to molecularly adsorbed HCOOH and to formate species. The band characteristic of molecularly adsorbed HCOOH (1675 cm⁻¹) disappeared in the spectrum of 1% Rh/TiO₂, while it could be detected in the case of 1% Au/TiO₂ at 383 K. The intensities of the bands due to adsorbed formate species changed in a smaller extent on 1% Au/TiO₂ than on 1% Rh/TiO₂ with the increase of the temperature.

A shoulder at 1710–1717 cm⁻¹ appeared on the spectra due to the adsorbed layer (Figs. 1 and 2), which could be

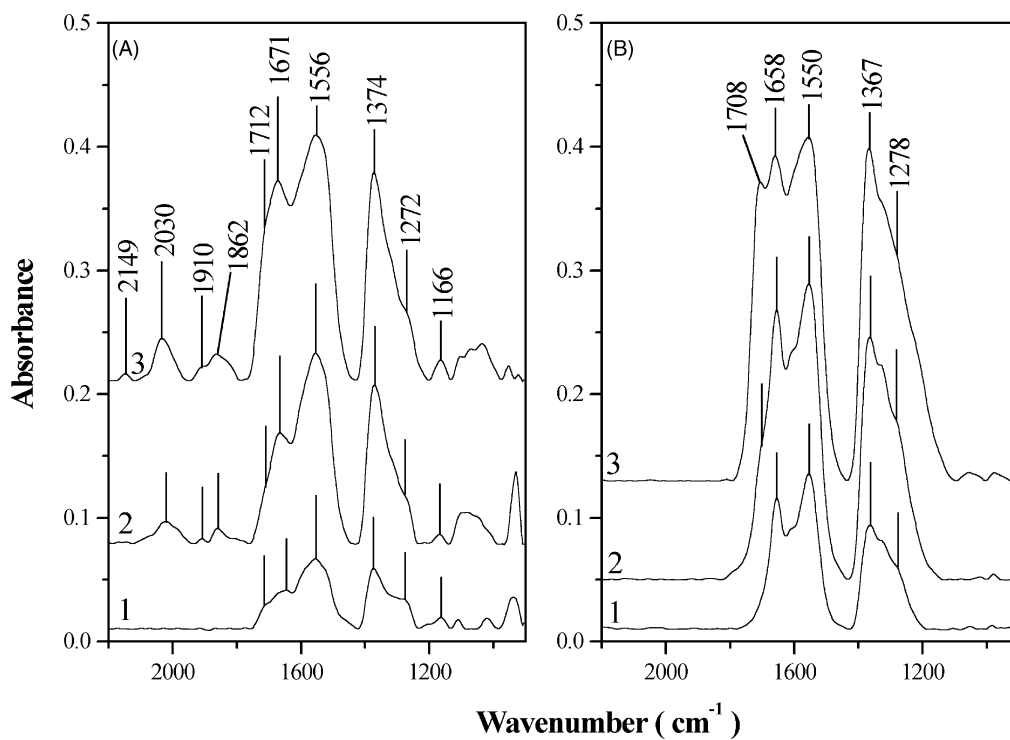


Fig. 1. Infrared spectra due to adsorbed layer formed at 300 K on reduced 1% Rh/TiO₂ (A) and on reduced 1% Au/TiO₂ (B) during the adsorption of HCOOH: (1) 0.01 Torr; (2) 0.1 Torr and (3) 1 Torr. Adsorption time was 5 min.

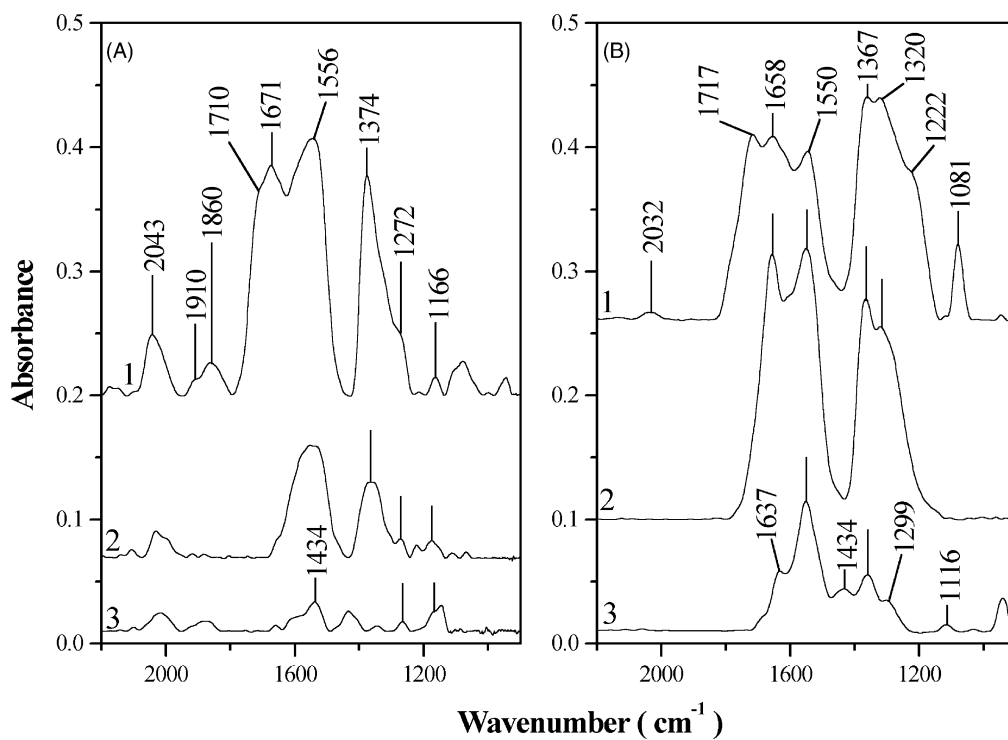


Fig. 2. Infrared spectra registered after 60 min adsorption of 1 Torr HCOOH at different temperatures on reduced 1% Rh/TiO₂: (A) and on reduced 1% Au/TiO₂ and (B) (1) 300 K; (2) 383 K and (3) 473 K.

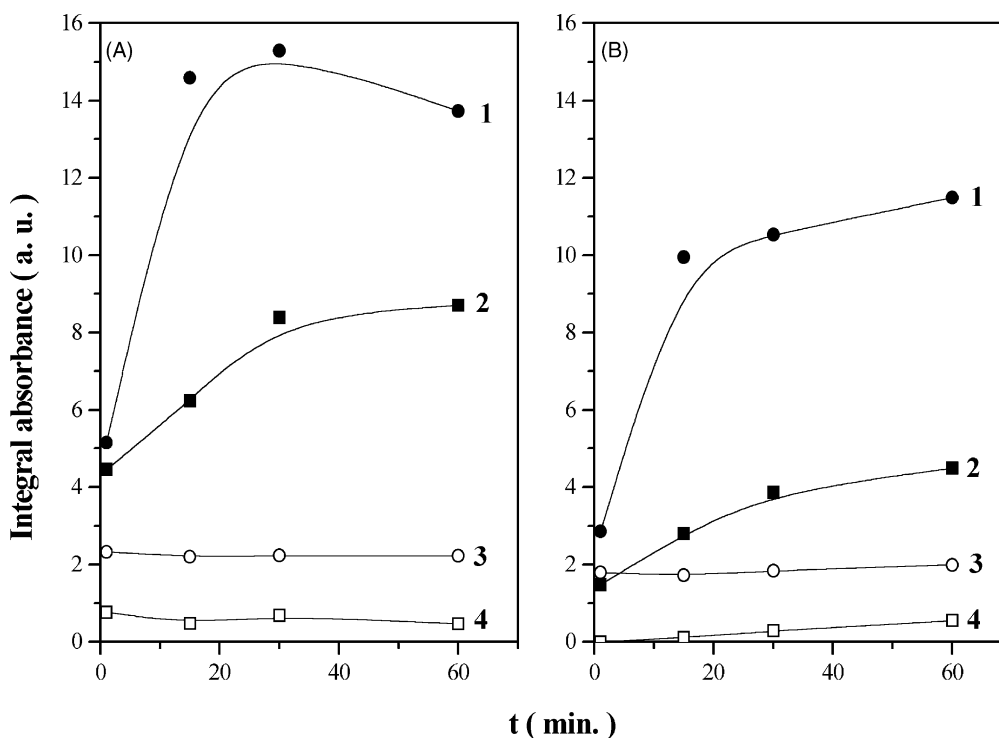


Fig. 3. Integrated absorbance values of the $1710\text{--}1717\text{ cm}^{-1}$ band determined during the adsorption of 1 Torr HCOOH at 300 K on: (1) 5% Pt/TiO₂; (2) 5% Au/TiO₂; (3) TiO₂ and (4) 5% Rh/TiO₂. (A) Oxidized surfaces and (B) reduced surfaces.

assigned to adsorbed formaldehyde ($\text{CH}_2\text{O}_{(a)}$). This shoulder disappeared when the HCOOH vapor was evacuated at the adsorption temperature(s). For the better determination of the integrated absorbance of this shoulder (i.e. the surface concentration of this species) the spectrum registered after evacuation at the adsorption temperature was subtracted from the spectra characteristic of the adsorbed layer being in equilibrium with HCOOH vapor. This subtraction resulted in the clear appearance of the $1710\text{--}1717\text{ cm}^{-1}$ band on the spectra, the integrated absorbance of which could be easily determined. The integrated absorbance values obtained for 5% metal/TiO₂ samples at 300 K are shown in Fig. 3. For comparison the data for TiO₂ and 5% Pt/TiO₂ (recently studied [10]) are also depicted.

Formaldehyde formed in the highest surface concentration on oxidized 5% Pt/TiO₂ at 300 K, and its surface concentration on oxidized surfaces decreased in the order of 5% Pt/TiO₂ > 5% Au/TiO₂ > TiO₂ > 5% Rh/TiO₂. After the reduction of the catalysts the integrated absorbances of the $1710\text{--}1717\text{ cm}^{-1}$ band were smaller than on the oxidized surfaces, the above order in surface concentration, however, has not been changed. A band due to formaldehyde in the adsorbed layer appeared at higher (383 and 473 K) adsorption temperatures only on TiO₂. The intensity of this band decreased with the increase of the adsorption temperature. On metal-containing catalysts (both on oxidized and reduced surfaces) the formaldehyde band was not observed in the adsorbed layer at 383 and 473 K.

During the above processes the changes in the gas phase were continuously detected by mass spectrometer. Special attention has been paid to the formation of the dehydrogenation products (H_2 and CO_2) and the dehydration products (H_2O and CO), respectively. While H_2 and CO_2 formed parallel in any experimental conditions, there was no direct correlation between the formation of H_2O and CO . In Fig. 4A and B data illustrating the above statement are shown, which were obtained during the interaction of HCOOH and reduced 5% metal/TiO₂ catalysts at 473 K.

Formaldehyde could be detected also in the gas phase during the interaction between HCOOH and the catalysts. Fig. 5 shows that the amount of formaldehyde in the gas phase depended on the nature of the metal and on the reaction temperature. At 300 K formaldehyde formed in greater amount on TiO₂ and 5% Pt/TiO₂, on 5% Au/TiO₂ and on 5% Rh/TiO₂, however, only a small quantity of formaldehyde was detected in the gas phase. The amount of gas phase formaldehyde decreased with the increase of the reaction temperature on TiO₂ and 5% Pt/TiO₂. At 383 and 473 K practically no gas phase formaldehyde formation was observed in the cases of 5% Au/TiO₂ and 5% Rh/TiO₂.

Interestingly, ethylene and a small amount of methane were detected among the gas phase products. The changes in the amount of ethylene showed great similarities to that of formaldehyde: the highest amount of ethylene was detected in the case of TiO₂ and 5% Pt/TiO₂, where the greatest amount of formaldehyde was obtained.

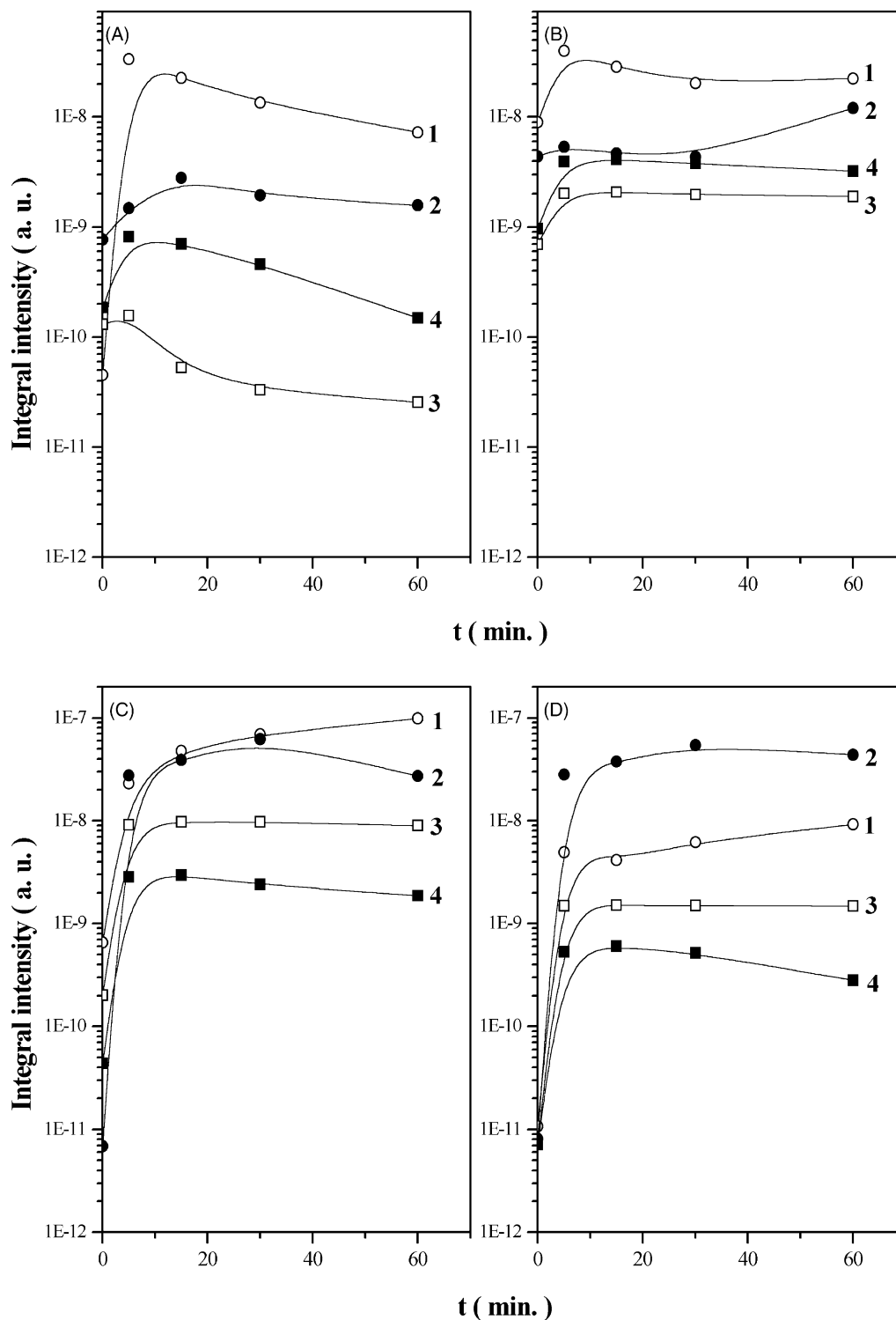


Fig. 4. Changes in the amount of gas phase products (calculated from MS data) during the reaction of HCOOH (1 Torr) on reduced catalysts at 473 K: (A) H₂O; (B) CO; (C) H₂ and (D) CO₂; (1) TiO₂; (2) 5% Pt/TiO₂; (3) 5% Rh/TiO₂ and (4) 5% Au/TiO₂.

4. Discussion

We collected the literature data on the vibrational frequencies and their assignments due to molecularly adsorbed HCOOH (Table 1) and due to formate species originating

from the dissociation of HCOOH (Table 2) on TiO₂ surfaces. Table 3 contains the characteristic bands of gaseous formaldehyde, as a possible product of HCOOH adsorption.

Taking into account the data of Tables 1–3 and the bands observed in this work (Table 4), it can be concluded

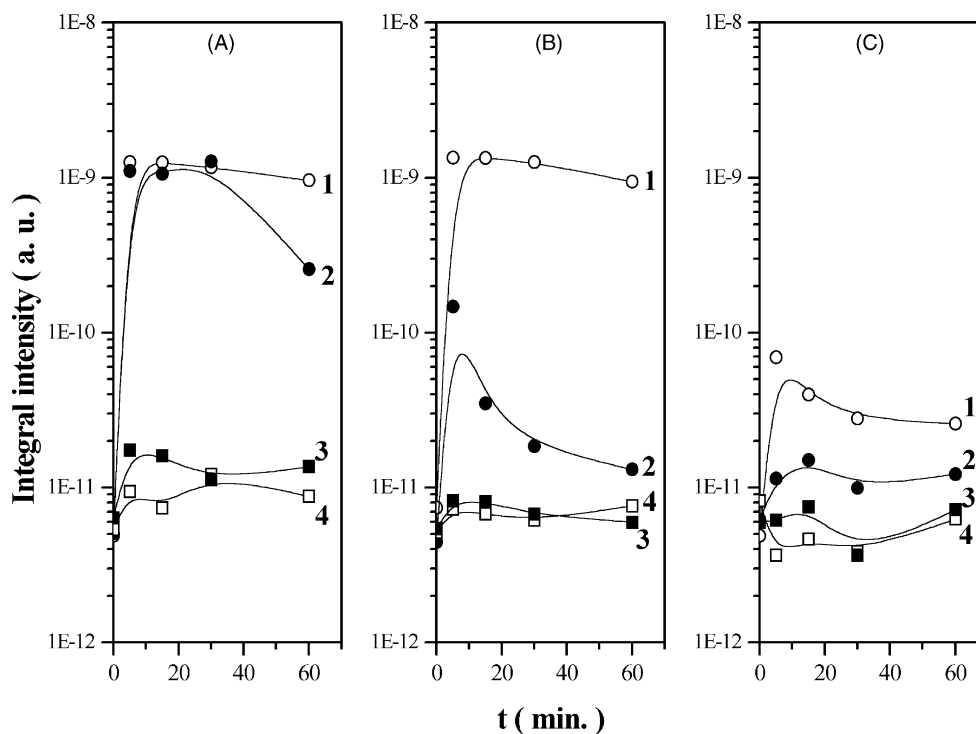


Fig. 5. Changes in the amount of gas phase formaldehyde during the reaction of HCOOH (1 Torr) on reduced catalysts: (A) at 300 K; (B) at 383 K and (C) at 473 K. (1) TiO₂; (2) 5% Pt/TiO₂; (3) 5% Au/TiO₂ and (4) 5% Rh/TiO₂.

Table 1
Vibrational frequencies (in cm⁻¹) of HCOOH gas and molecularly adsorbed HCOOH

Assignment	HCOOH gas [17]	HCOOH _(a) on TiO ₂ powder [18]	HCOOH _(a) on TiO ₂ powder [19]	HCOOH _(a) on TiO ₂ (1 1 0) [7,20] ^a
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 mode 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) [18]	TiO ₂ (powder) [19]	TiO ₂ (1 1 0) [20]	TiO ₂ (1 1 0) [7]
Combination of ν_a (OCO) and CH deform	2977 2952		2928	2920
ν (CH)	2872			
ν_a (OCO) + δ_a (CH)	2754			
ν_a (OCO)	1552 1537	1560 1553	1524	
δ (CH) or γ (OCO)	1413 1386	1410 1381 1379	1379	1365
ν_s (OCO)	1370 1359	1356		

Table 3
Characteristic bands (in cm^{-1}) of gaseous formaldehyde [17]

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

that besides the bands due to molecularly adsorbed HCOOH (2928, 1671–1658 cm^{-1} and 1072–1081 cm^{-1}) and adsorbed formate species (2962–2955 cm^{-1} , 2872–2868 cm^{-1} , 2734–2764 cm^{-1} , 1556–1550 cm^{-1} and 1374–1367 cm^{-1}) bands due to formaldehyde (1712–1717 cm^{-1} , 1272–1278 cm^{-1} and 1166 cm^{-1}) appeared on the spectra characteristic of the adsorbed layer produced by HCOOH adsorption on Rh/TiO₂ and Au/TiO₂ catalysts.

As all these bands appeared on the spectra of TiO₂ alone during HCOOH adsorption [10], the question emerged on the role of metal in this surface reaction. Experimental data and conclusions have been presented on the facile deoxygenation of HCOOH resulting in the formation of formaldehyde on Pt sites. If the suggestion on the HCOOH deoxygenation on metal sites were valid, the amount of formaldehyde formed in this process should be influenced by the nature of the metals. Fig. 3 of this work would strengthen the validity of this suggestion, as the amount of formaldehyde in the adsorbed layer depended on the nature of the metals. At 300 K formaldehyde formed in the highest concentration on Pt/TiO₂, and its amount in the adsorbed layer decreased in the order of Au/TiO₂ > TiO₂ > Rh/TiO₂. This order might be connected with the ability of different metals (catalysts) in extracting oxygen from a molecule.

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

Assignment	Rh/TiO ₂	Au/TiO ₂
ν_a (OCO) + δ (CH) in HCOO _(a)	2962	2955
ν (CH) in HCOOH _(a)	2928	2928
ν (CH) in HCOO _(a)	2872	2868
ν_s (OCO) + δ (CH) in HCOO _(a)	2734	2764
Rh ³⁺ -CO [22]	2149	
M ⁰ -CO [22]	2030	2032
(Rh ⁰) ₂ -CO [22]	1910	
(Rh ⁰) ₃ -CO [22]	1862	
ν (CO) in H ₂ CO _(a)	1712	1717
ν (CO) in HCOOH _(a)	1671	1658
ν_a (OCO) in HCOO _(a)	1556	1550
ν_s (OCO) in HCOO _(a)	1374	1367
(CH ₂) rocking in H ₂ CO _(a)	1272	1278
(CH ₂) wagging in H ₂ CO _(a)	1166	
(CH) bend in HCOOH _(a)	1072	1081

^a This work.

A part of formaldehyde formed in the adsorbed layer desorbs from the catalyst surfaces: its quantity in the gas phase depends on the nature of the metals and on the adsorption temperature (Fig. 5). The amount of formaldehyde in the gas phase was the highest at all temperatures in the case of TiO₂. This finding can be explained by the presence of metal, as on metal sites formaldehyde decomposes into gas phase CO and/or CO adsorbed on metal sites.

The appearance of the 2150 cm^{-1} band on the spectra of Rh/TiO₂ (Figs. 1A and 2A) due to Rh³⁺-CO surface species can be accepted as an indirect proof of the deoxygenation of HCOOH causing the oxidation of the (originally reduced) metal sites. In the case of Au/TiO₂ band characteristic of adsorbed CO was not observed, or it was hardly detected. It should be taken into account that CO adsorbs very weakly on oxide-supported Au catalysts [13].

In harmony with the literature [7] we also observed that the development of water and carbon monoxide proved to be not directly linked (Fig. 4), thus the simple unimolecular reaction proposed [5] for the H₂O and CO formation (in the dehydration of HCOOH) could be excluded.

Based upon the data previously [10] published and shown in the present work we suppose that the main source of CO formation is the decomposition of formaldehyde produced in the deoxygenation of HCOOH. The surface active centers for the reduction (deoxygenation) of HCOOH may be Ti³⁺ formed during the pretreatment of TiO₂ and/or metal sites (Rh and Au surface atoms in the present case).

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