

# FTIR and mass spectrometric studies on the interaction of formaldehyde with TiO<sub>2</sub> supported Pt and Au catalysts

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## Abstract

The interaction of formaldehyde with Pt/TiO<sub>2</sub> and Au/TiO<sub>2</sub> catalysts was investigated at 300–473 K by Fourier transform infrared spectroscopy and mass spectrometry. The effects of the pretreatments and the metal content of the catalysts, as well as the effects of the reaction temperature on the formation of the surface species and on the gas phase products were studied. Molecularly adsorbed formaldehyde, formic acid, formate, dioxymethylene and polyoxymethylene surface species are formed during formaldehyde adsorption at 300–473 K. The main gas phase products were H<sub>2</sub> and CO; their amounts increased with the increase of the metal content of the catalysts and with the increase of the reaction temperature. Gas phase ethylene, acetylene, as well as formic acid were detected on pure TiO<sub>2</sub>. On metal-containing TiO<sub>2</sub> no ethylene, acetylene and formic acid were observed, which could be connected with the limited surface concentration of oxygen vacancies on these surfaces.

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**Keywords:** Formaldehyde adsorption and reactions; Pt/TiO<sub>2</sub> and Au/TiO<sub>2</sub> catalysts; Surface species studied by FTIR; Gas phase products detected by MS

## 1. Introduction

As formaldehyde is either the product or an intermediate of important organic catalytic reactions [1–6], its adsorption and reaction have been frequently studied on single crystal surfaces of metal oxides [7–11], on polycrystalline oxides [12–14] and on single crystal metal surfaces [13,15–17].

Recently, we have found [18,19] that formaldehyde would play a more decisive role in the catalytic reactions of formic acid: it was postulated that the main source of CO in the catalytic HCOOH transformation may be the thermal decomposition of formaldehyde produced by the deoxygenation of HCOOH. This finding would interpret the experimental fact [20] that the formations of water and CO (the products of the classical dehydration route of HCOOH decomposition) are not to be linked.

A previous study of the interaction between formaldehyde and TiO<sub>2</sub> supported Rh catalysts [21] seemed to strengthen the above idea: the main gas phase products of this inter-

action were CO and hydrogen. In harmony with the former data the complexity of HCOH adsorption has been deduced.

As a continuation of our earlier studies in this work we present the experimental findings of the adsorption and reactions of HCOH on TiO<sub>2</sub> supported Pt and Au catalysts.

## 2. Experimental

TiO<sub>2</sub> was the product of Degussa (P25, 50 m<sup>2</sup>/g). The 1 and 5 wt.% Pt/TiO<sub>2</sub> catalysts were prepared by impregnating TiO<sub>2</sub> with an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub>·3H<sub>2</sub>O (Reanal). The impregnated powders were dried at 383 K for 3 h. TiO<sub>2</sub> supported Au catalysts (1 and 5 wt.%) were made by a deposition–precipitation method. Chloroauric acid (HAuCl<sub>4</sub>(aq) p.a. 49% Au, Fluka AG) was first dissolved in triply distilled water. After the pH of the HAuCl<sub>4</sub> aqueous solution was adjusted to pH 7.5 by adding 1 M NaOH solution, the fine powder of the 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

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with distilled water repeatedly, dried at 353 K and then calcined in air at 573 K for 4 h. Formaldehyde was prepared by the thermal decomposition of paraformaldehyde (Reanal) at 453–473 K.

For IR studies the catalyst powders were pressed onto a Ta-mesh (30 mm × 10 mm, 5 mg/cm<sup>2</sup>). 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<sup>−7</sup> Torr): (a) heated in 1 Torr of O<sub>2</sub> (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<sub>2</sub> (133.3 Pa) up to 573 K and it was kept at this temperature for 1 h. Steps (a) and (b) were followed by degassing at the same temperature for 30 min and by cooling the sample to the temperature of the experiment. The dispersity of the reduced sample was 29% for 1% Pt/TiO<sub>2</sub> and 27% for 5% Pt/TiO<sub>2</sub> determined by H<sub>2</sub> adsorption at room temperature. The dispersion of Au was measured by CO adsorption following the method suggested by Shastri et al. [22]. Whereas the dispersion of Au was relatively high (46%) for 1% Au/TiO<sub>2</sub>, this value decreased to 7% for 5% Au/TiO<sub>2</sub> [23]. The average particle sizes were calculated on the basis of the dispersity data [24,25]: it was 3.1 nm for 1% Pt/TiO<sub>2</sub> and 3.3 nm for 5% Pt/TiO<sub>2</sub> and that of Au was 1.96 nm on 1% Au/TiO<sub>2</sub> and 12.9 nm on 5% Au/TiO<sub>2</sub>.

Infrared spectra were recorded with a Genesis (Mattson) FTIR spectrometer with a wave number accuracy of ±4 cm<sup>−1</sup>. Typically 136 scans were collected. The whole optical path was purged by CO<sub>2</sub>- and H<sub>2</sub>O-free air generated by a Balston 75-62 FTIR 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  $5 \times 10^{-6}$  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

#### 3.1. Infrared studies

During the adsorption of 0.01 Torr formaldehyde at 300 K the bands at 2969, 2926, 2864, 2792, 2044, 1706, 1588, 1446, 1394, 1301, 1265, 1124, 1067, 963 and 936 cm<sup>−1</sup> appeared on the spectra of oxidized 1% Pt/TiO<sub>2</sub>. The increase of the formaldehyde pressure caused the appearance of new bands (2798, 2758, 1656, 1403, 1251 and 1158–1166 cm<sup>−1</sup>), resulted in the shifts of some bands (the 2926 cm<sup>−1</sup> band shifted to 2913 cm<sup>−1</sup>, the 2044 cm<sup>−1</sup> band to 2062 cm<sup>−1</sup> and the 1124 cm<sup>−1</sup> band shifted to 1116 cm<sup>−1</sup>) and led to the overall increase of the bands intensities (Fig. 1). Most of the bands listed above were detected on reduced 1% Pt/TiO<sub>2</sub> with somewhat smaller intensities and with similar shifts. The most striking difference between the oxidized and the reduced surfaces was the nearly complete absence of the band at 2100–2000 cm<sup>−1</sup> on the spectra of reduced 1% Pt/TiO<sub>2</sub>.

Spectra registered at 300 K during the adsorption of 0.01–1 Torr formaldehyde on oxidized 1% Au/TiO<sub>2</sub> (Fig. 2) show some differences from that observed on oxidized 1% Pt/TiO<sub>2</sub>: (i) there is no band in the range of 2100–2000 cm<sup>−1</sup> on the spectra of oxidized 1% Au/TiO<sub>2</sub>; (ii) at the lowest formaldehyde pressure a band at 1698 cm<sup>−1</sup> appeared, which shifted to 1710 cm<sup>−1</sup> with the increase of the pressure and (iii) instead of the 1656 cm<sup>−1</sup> band on 1% Pt/TiO<sub>2</sub> a band at 1629 cm<sup>−1</sup> was observed on 1% Au/TiO<sub>2</sub>.

The intensities of the above bands were smaller on the spectra of reduced 1% Au/TiO<sub>2</sub>, and—contrary to reduced 1% Pt/TiO<sub>2</sub>—small bands at 2078 and 2030 cm<sup>−1</sup> were detected in the 2100–2000 cm<sup>−1</sup> region.

Next the adsorption of formaldehyde (1 Torr) was investigated at different temperatures. The spectra of reduced 1% Pt/TiO<sub>2</sub> registered at different temperatures are presented in Fig. 3. The band at 2912 and 2758 cm<sup>−1</sup> disappeared and new bands at 2930, 2829 and 2780 cm<sup>−1</sup> appeared in the C–H stretching region, when the adsorption temperature was increased from 300 to 383 K. Bands observed at 383 K were also detected at 473 K with smaller intensities. Among the bands registered in the lower wave number range, the bands at 1411, 1303, 1253, 1170 and 1116 cm<sup>−1</sup> disappeared at 383–473 K. Very small bands at 2090 and 2022 cm<sup>−1</sup> were observed at 300–383 K, at 473 K only the 2090 cm<sup>−1</sup> band appeared. The bands at 1690 and 1650 cm<sup>−1</sup> were constantly present on the spectra at 300–473 K.

The oxidation of 1% Pt/TiO<sub>2</sub> did not modify the spectral features of the C–H stretching region observed on reduced catalyst at 300–473 K. At lower wave numbers, however, some differences were experienced: only one band at 2055 cm<sup>−1</sup> appeared in the 2100–2000 cm<sup>−1</sup> range in formaldehyde adsorption on the oxidized surface at 300 K, the position of which shifted to lower wave numbers (2042–2032 cm<sup>−1</sup>) with the increase of the adsorption temperature. Another difference between the oxidized and the

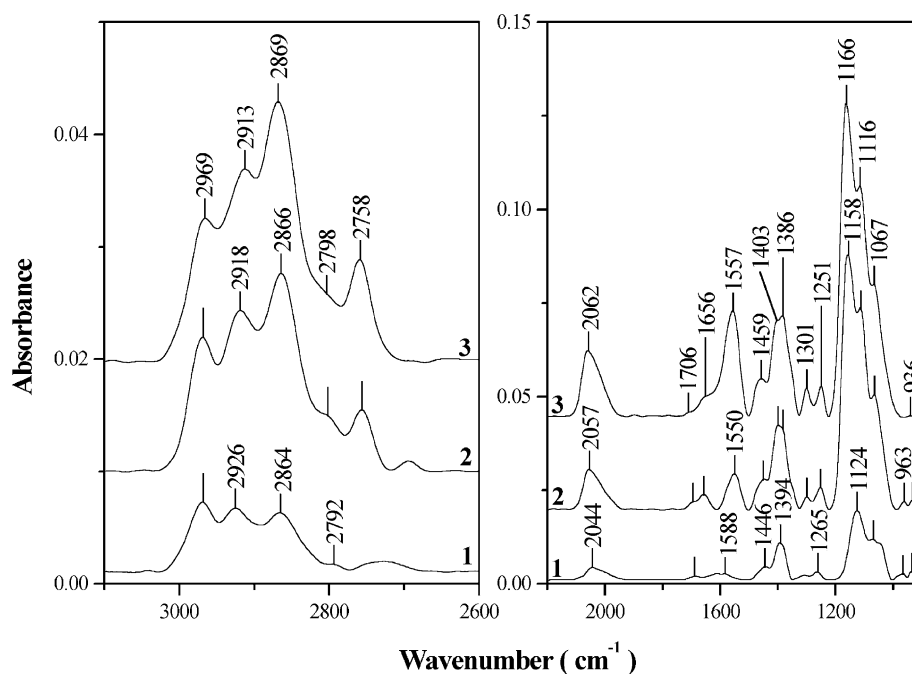


Fig. 1. The effect of formaldehyde pressure on the spectra registered at 300 K on oxidized 1% Pt/TiO<sub>2</sub> (adsorption time 1 min): (1) 0.01 Torr, (2) 0.1 Torr and (3) 1 Torr.

reduced surfaces is that the band at 1695 cm<sup>-1</sup> appeared only at 473 K in the case of oxidized 1% Pt/TiO<sub>2</sub>.

Spectra similar in many respects were registered during the adsorption of CH<sub>2</sub>O (1 Torr) at different temperatures on reduced 1% Au/TiO<sub>2</sub> (Fig. 4). Instead of the 2973 cm<sup>-1</sup> band detected at 300 K on 1% Au/TiO<sub>2</sub> a band at 2963 cm<sup>-1</sup> was observed at 383 K, which disappeared at 473 K. Further

differences are that the 1640 cm<sup>-1</sup> band was more intense, the band at 1552 cm<sup>-1</sup> was smaller on 1% Au/TiO<sub>2</sub> than on 1% Pt/TiO<sub>2</sub>.

Spectra observed on oxidized 1% Au/TiO<sub>2</sub> did not differ considerably from those taken on the reduced catalyst.

The increase of the Pt content did not affect the spectral features of the 3100–2600 cm<sup>-1</sup> range registered on 1%

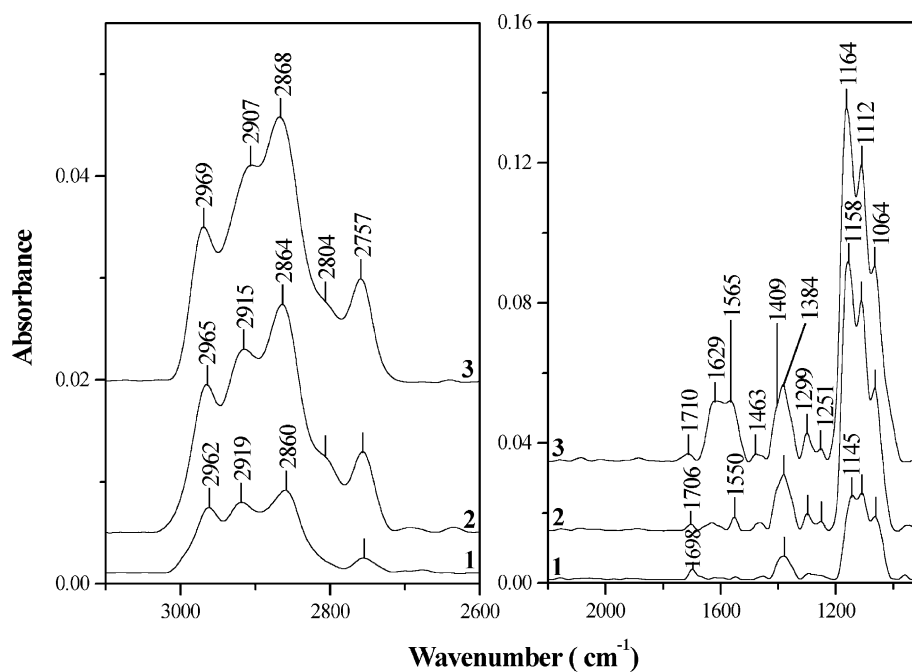


Fig. 2. The effect of formaldehyde pressure on the spectra registered at 300 K on oxidized 1% Au/TiO<sub>2</sub> (adsorption time 1 min): (1) 0.01 Torr, (2) 0.1 Torr and (3) 1 Torr.

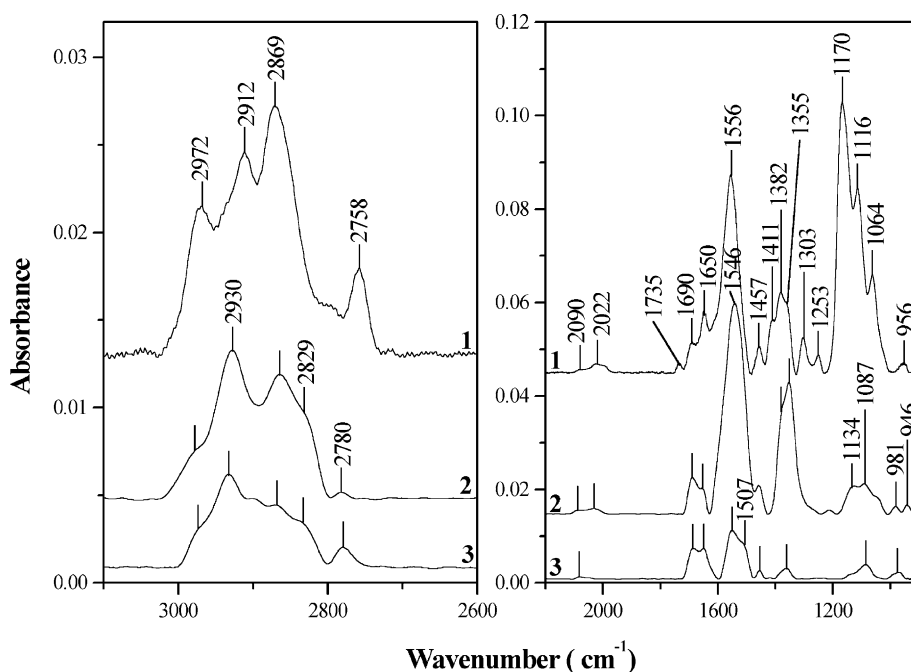


Fig. 3. IR spectra observed during the adsorption of 1 Torr formaldehyde at different temperatures for 1 h on reduced 1% Pt/TiO<sub>2</sub> (the spectra were taken at the adsorption temperature): (1) 300 K, (2) 383 K and (3) 473 K.

Pt/TiO<sub>2</sub> as a function of formaldehyde pressure. In the region of 2200–900 cm<sup>-1</sup>, however, some obvious differences were detected. On oxidized 5% Pt/TiO<sub>2</sub> the intensity of the band at 2053 cm<sup>-1</sup> proved to be several times higher than on 1% Pt/TiO<sub>2</sub>, already in the adsorption of 0.01 Torr formaldehyde at 300 K (Fig. 5A). Its position shifted to higher wave numbers with the increase of formaldehyde pressure. Bands

at 1835, 1690 and 1471 cm<sup>-1</sup> were observed on oxidized 5% Pt/TiO<sub>2</sub>; these bands were not detected on oxidized 1% Pt/TiO<sub>2</sub>. Another difference is that the 1650 cm<sup>-1</sup> band was more intense on oxidized 5% Pt/TiO<sub>2</sub>, than on oxidized 1% Pt/TiO<sub>2</sub>. After the reduction of 5% Pt/TiO<sub>2</sub> a small band at 2011 cm<sup>-1</sup> appeared in 0.01 Torr formaldehyde at 300 K (Fig. 5B). In 0.1 Torr formaldehyde two bands at 2067

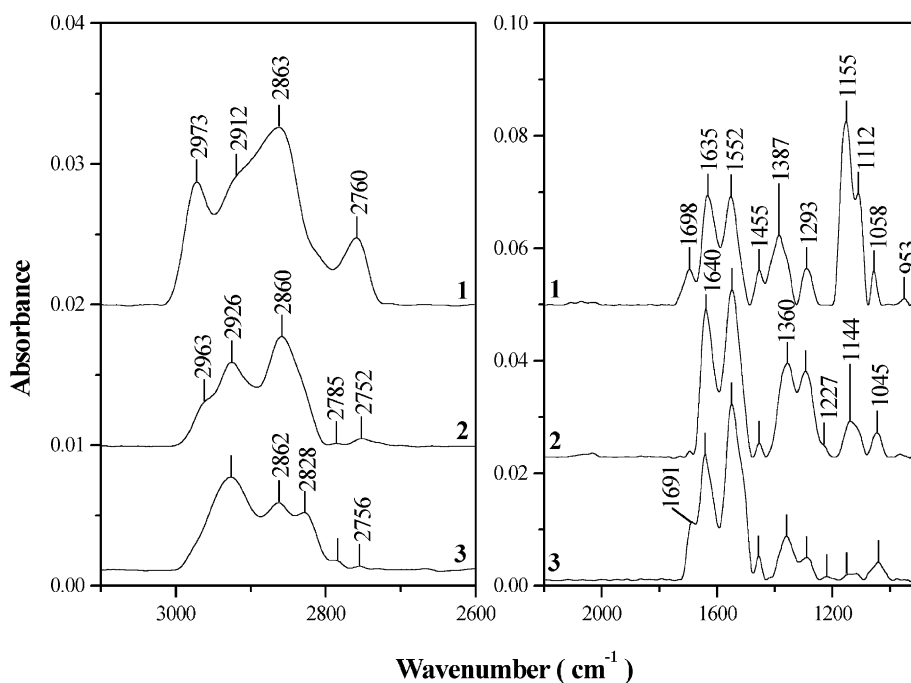


Fig. 4. IR spectra observed during the adsorption of 1 Torr formaldehyde at different temperatures for 1 h on reduced 1% Au/TiO<sub>2</sub> (the spectra were taken at the adsorption temperature): (1) 300 K, (2) 383 K and (3) 473 K.

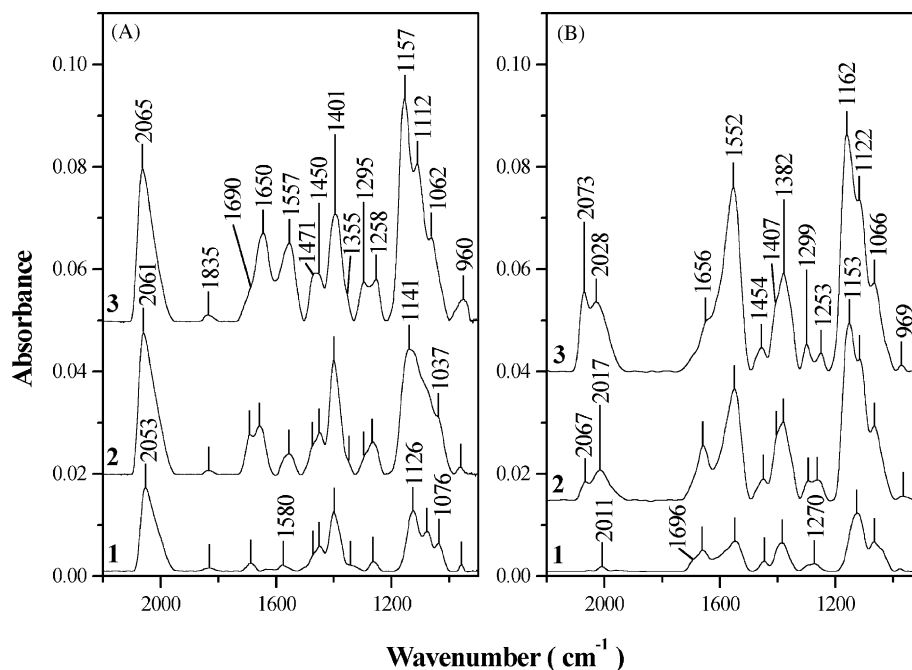


Fig. 5. The effect of formaldehyde pressure on the spectra registered at 300 K on oxidized (A) and reduced (B) 5% Pt/TiO<sub>2</sub>: 1–0.01, 2–0.1 and 3–1 Torr. The adsorption time was 1 min.

and 2017 cm<sup>-1</sup> were detected, which shifted to 2073 and 2028 cm<sup>-1</sup> with the further increase of the formaldehyde pressure to 1 Torr. These bands appeared with significantly higher intensities, as did the 2090–2022 cm<sup>-1</sup> band pair on reduced 1% Pt/TiO<sub>2</sub>. The increase of the adsorption temperature both on the oxidized and the reduced 5% Pt/TiO<sub>2</sub> led to qualitatively similar spectral changes, as observed in the

case of 1% Pt/TiO<sub>2</sub>. The only difference was the detection of the bands in the range of 2200–2000 cm<sup>-1</sup> even at 473 K.

Spectral changes observed in the C–H stretching region on reduced 5% Au/TiO<sub>2</sub> due to the increase of formaldehyde pressure and to that of the adsorption temperature show great similarities to those registered in the case of 5% Pt/TiO<sub>2</sub> catalyst. Bands appeared at 2128, 2081 and 2044 cm<sup>-1</sup> on

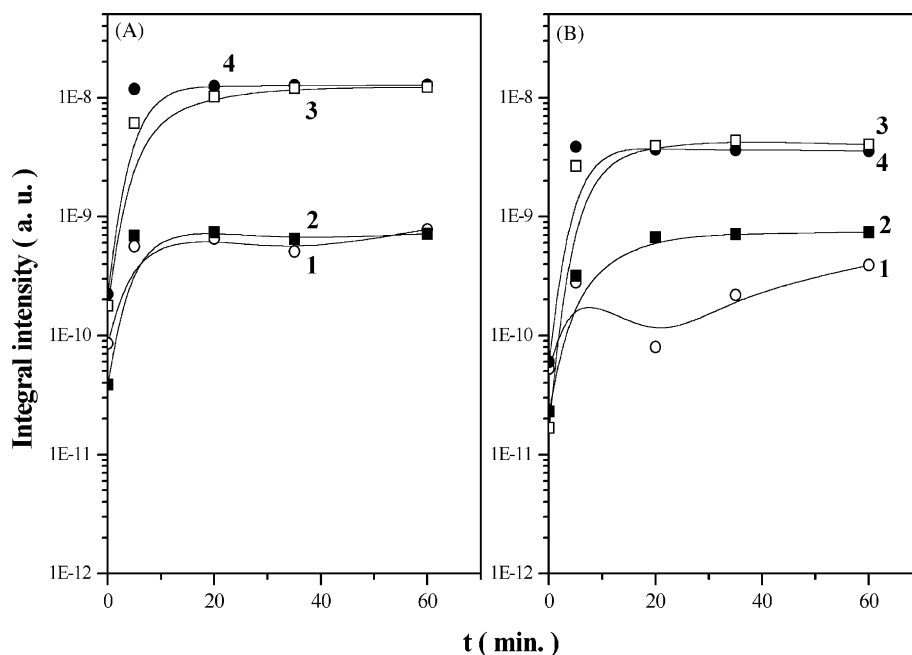


Fig. 6. Formation of H<sub>2</sub> (A) and CO (B) in the gas phase (detected by mass spectrometer) in the reaction of 1 Torr formaldehyde with reduced catalysts at 473 K: (1) TiO<sub>2</sub>, (2) 5% Au/TiO<sub>2</sub>, (3) 5% Pt/TiO<sub>2</sub> and (4) 5% Rh/TiO<sub>2</sub>.

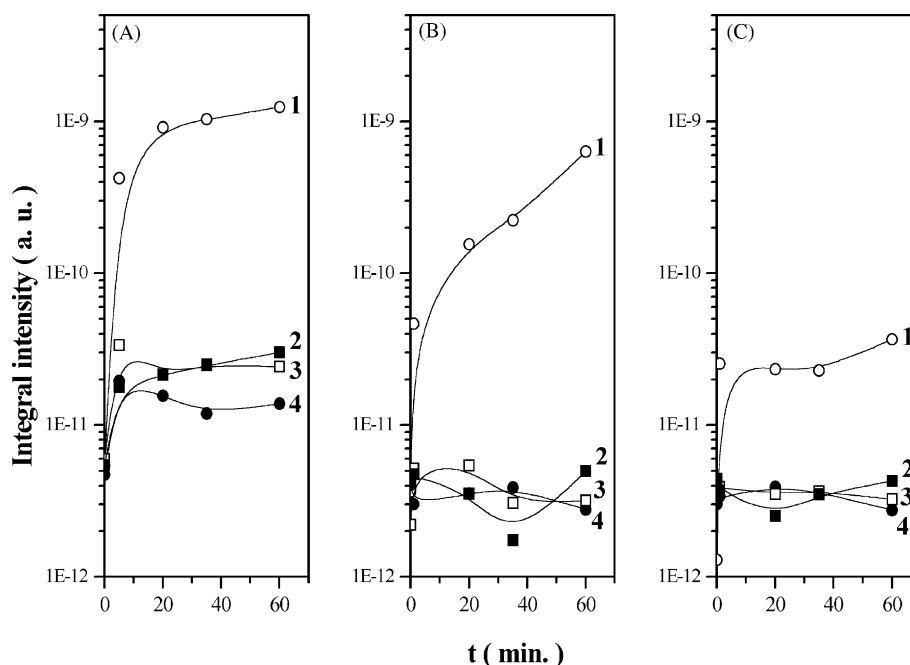


Fig. 7. Formation of gas phase ethylene (A), acetylene (B) and formic acid (C) (detected by mass spectrometer) in the reaction of 1 Torr formaldehyde on oxidized catalysts at 473 K: (1)  $\text{TiO}_2$ , (2) 5%  $\text{Au/TiO}_2$ , (3) 5%  $\text{Pt/TiO}_2$  and (4) 5%  $\text{Rh/TiO}_2$ .

5%  $\text{Au/TiO}_2$ , however, they were much less intense than the bands registered between 2000 and  $2200\text{ cm}^{-1}$  on 5%  $\text{Pt/TiO}_2$ .

### 3.2. Mass spectrometric investigations

Parallel with the registration of the IR spectra the changes in the product distribution of the gas phase were monitored by MS. The main products of the formaldehyde decomposition were  $\text{H}_2$  and  $\text{CO}$ . The amounts of these products depended on the metal content and the reaction temperature: the higher were these parameters, the higher were the amounts of  $\text{H}_2$  and  $\text{CO}$ . The pretreatments of the catalysts (oxidation or reduction) did not basically modify the above features. For comparison the data of  $\text{H}_2$  and  $\text{CO}$  formations measured at 473 K on reduced 5% metal/ $\text{TiO}_2$  catalysts were plotted in Fig. 6 (data previously published for  $\text{Rh/TiO}_2$  are also included). The most effective catalysts in forming  $\text{H}_2$  and  $\text{CO}$  proved to be  $\text{Pt/TiO}_2$  and  $\text{Rh/TiO}_2$ ;  $\text{Au/TiO}_2$  catalyst produces less  $\text{H}_2$  and  $\text{CO}$ .

There was practically no  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  formation on 1 and 5% metal/ $\text{TiO}_2$  catalysts (both on oxidized and reduced) during their interaction with formaldehyde at 300–473 K. On oxidized and reduced  $\text{TiO}_2$ , however,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_2$  were detected in the gas phase: their quantities increased with the increase of the reaction temperature. Small amount of methane was detected among the gas phase products, the changes of its amount with the experimental parameters, however, were not significant.

$\text{HCOOH}$  production was not observed on Pt- and Au-containing catalysts. On pure  $\text{TiO}_2$  formic acid appeared

among the gas phase products: on the oxidized support the amount of  $\text{HCOOH}$  increased, while on reduced  $\text{TiO}_2$  its quantity decreased with the increase of the reaction temperature. Fig. 7 shows the data obtained during the interaction of formaldehyde with different oxidized catalysts at 473 K illustrating the above statements.

## 4. Discussion

The literature assignments of the bands due to formaldehyde molecular species, due to dioxymethylene and polyoxymethylene species are presented in Tables 1 and 2.

Based upon the literature data it can be concluded that during the interaction of formaldehyde with  $\text{Pt/TiO}_2$  and  $\text{Au/TiO}_2$  catalysts molecularly adsorbed formaldehyde ( $2798\text{--}2804$ ,  $1706\text{--}1710$ ,  $1251\text{--}1253$  and  $1134\text{--}1170\text{ cm}^{-1}$ ), formate ( $2962\text{--}2973$ ,  $1552\text{--}1556$  and  $1382\text{--}1387\text{ cm}^{-1}$ ), formic acid ( $1690\text{--}1698\text{ cm}^{-1}$ ), dioxymethylene ( $2860\text{--}2869$ ,  $2757\text{--}2760$ ,  $1455\text{--}1463$ ,  $1403\text{--}1411$ ,  $1301\text{--}1303$ ,  $1112\text{--}1116$  and  $1058\text{--}1067\text{ cm}^{-1}$ ) and polyoxymethylene ( $2912\text{--}2930$  and  $936\text{--}967\text{ cm}^{-1}$ ) surface species formed. Formaldehyde adsorbs molecularly through a lone pair donation from the oxygen of carbonyl to Lewis acid sites (in the present case  $\text{Ti}^{+4}$  surface cations) [33]. As a result the carbon of the carbonyl becomes more electrophilic, favoring an attack from a nucleophilic surface oxygen ion to form dioxymethylene (DOM,  $\text{H}_2\text{CO}_{2(\text{a})}$ ) species [35]. Surface polymerization of dioxymethylene results in the formation of polyoxymethylene (POM). These results are in harmony with the previous findings [12,21]. No bands due to



Table 1  
Observed wave numbers ( $\text{cm}^{-1}$ ) of formaldehyde molecular species

Assignment	Gas [26,27,28]	Solid monomer [28]	Condensed on Ag [29]	On $\text{Al}_2\text{O}_3$ at 170 K [12]
$\nu_{\text{as}}(\text{CH}_2)$	2843.3	2843	2850	2885
$\nu_{\text{s}}(\text{CH}_2)$	2782.5	2783	nr	2818
$\delta(\text{CH}_2) + \omega(\text{CH}_2)$	2719.2			2725
$\nu(\text{CO})$	1746.1	1746	1710	1718
$\delta(\text{CH}_2)$	1500.1	1500	1490	1498, 1485
$\omega(\text{CH}_2)$	1249.3	1249/1167	1250	1252
$\gamma(\text{CH}_2)$	1167.1			

methoxide and methylformate were detected in the present study, which shows that—contrary to some recent data [12,34,35]—the hydride transfer between two dioxymethylene species resulting in  $\text{CH}_3\text{O}_{(\text{a})}$  and  $\text{HCOO}_{(\text{a})}$  (net Cannizaro disproportionation), as well as the reaction of two molecularly adsorbed formaldehyde species resulting in the formation of  $\text{HCOOCH}_3_{(\text{a})}$  do not occur on these catalysts. As no methoxide species could be detected in the adsorbed layer, it might be supposed that not only the Cannizaro-type disproportionation results in surface formate. Hydride transfer inside the dioxymethylene species could lead to the formation of formic acid ( $1690\text{--}1698\text{ cm}^{-1}$ ), the dissociation of which may also cause the appearance of the bands due to surface formate (Table 3).

At 300 K bands due to dioxymethylene species were dominant on the spectra of Pt/TiO<sub>2</sub> and Au/TiO<sub>2</sub> catalysts. With the increase of the adsorption temperature the intensities of the bands due to DOM decreased, possibly due to the surface reactions producing gas phase products. The main gas phase products were H<sub>2</sub> and CO.

The presence of metals on the titania surface enhances the amount of the gas phase H<sub>2</sub> and CO (Fig. 6). The highest amounts of H<sub>2</sub> and CO were produced on Rh/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> catalysts. Au/TiO<sub>2</sub> proved to be less active than Rh/TiO<sub>2</sub> and Pt/TiO<sub>2</sub>, the amount of H<sub>2</sub> and CO measured on Au/TiO<sub>2</sub>, however, were higher than on pure TiO<sub>2</sub>. This obvious correlation leads to the conclusion that the most appropriate surface sites are surface metal centers for the decomposition of formaldehyde into H<sub>2</sub> and CO. A part of CO

formed in the formaldehyde decomposition adsorbs on the metal sites; the position of the band(s) due to adsorbed CO characterizes the oxidation state and/or the surface structure of the metal. The detailed analysis of the CO bands on supported Pt catalysts can be found elsewhere [36], here we only draw the attention to the nearly complete absence of the bands due to adsorbed CO on reduced 1% Pt/TiO<sub>2</sub> (Fig. 3), and to their dramatic decrease on reduced 5% Pt/TiO<sub>2</sub> (comparison of Fig. 5A and B). These features may be due to the decoration of Pt crystallites by TiO<sub>x</sub> occurring in the reductive pretreatment of Pt/TiO<sub>2</sub> catalysts [37,38]. In the case of Au/TiO<sub>2</sub> bands characteristic of adsorbed CO were hard to detect. It should be taken into account that CO adsorbs very weakly on oxide-supported Au catalysts [22].

All these data are in harmony with the recent suggestion [18,19] that the main source of CO formation in the catalytic transformation of HCOOH may be the thermal decomposition of formaldehyde produced by the deoxygenation of HCOOH.

The formation of C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and HCOOH was observed only on pure TiO<sub>2</sub>, on which oxygen vacancies produced in the pretreatments are present in high surface concentration. It is very possible that the adsorption of formaldehyde with its O-end on the oxygen vacancies and the consecutive rupture of the C–O bond leads to the formation of CH<sub>2(a)</sub> on pure

Table 2  
Characteristic bands (in  $\text{cm}^{-1}$ ) of dioxymethylene (DOM) and polyoxymethylene (POM) species

DOM		POM	
Assignment	In $\text{H}_2\text{C}(\text{OCD}_3)_2$ [30,31]	Assignment	Hexagonal POM [32]
$\nu_{\text{as}}(\text{CH}_2)$	2945	$\nu(\text{CH}_2)$	2984, 2920
$2\delta(\text{CH}_2)$	2932		
$\nu_{\text{s}}(\text{CH}_2)$	2882		
$2\omega(\text{CH}_2)$	2770		
$\delta(\text{CH}_2)$	1473	$\delta(\text{CH}_2)$	1471, 1384
$\tau(\text{CH}_2)$	1302	$\tau(\text{CH}_2)$	1290
$\rho(\text{CH}_2)$	1186	$\rho(\text{CH}_2)$	1238
$\nu(\text{C–O})$	1138, 1114, 1086, 858	$\nu(\text{C–O})$	1098, 936, 897

Table 3  
Bands (in  $\text{cm}^{-1}$ ) observed in the present study and their possible assignments

Assignment	Pt/TiO <sub>2</sub>	Au/TiO <sub>2</sub>
$\nu(\text{OCO}) + \delta(\text{CH})$ in $\text{HCOO}_{(\text{a})}$	2969–2972	2962–2973
$\nu(\text{CH}_2)$ in POM	2912–2930	2912–2926
$\nu_{\text{s}}(\text{CH}_2)$ in DOM	2869	2860–2868
$\nu_{\text{s}}(\text{CH}_2)$ in $\text{H}_2\text{CO}_{(\text{a})}$	2798	2804
$2\omega(\text{CH}_2)$ in DOM	2758	2757–2760
$\nu(\text{CO})$ in $\text{H}_2\text{CO}_{(\text{a})}$	1706	1706–1710
$\nu(\text{CO})$ in $\text{HCOOH}_{(\text{a})}$	1690	1698
$\nu_{\text{a}}(\text{OCO})$ in $\text{HCOO}_{(\text{a})}$	1556	1552–1565
$\delta(\text{CH}_2)$ in DOM	1457–1459	1455–1463
$\omega(\text{CH}_2)$ in DOM	1403–1411	1409
$\nu_{\text{s}}(\text{OCO})$ in $\text{HCOO}_{(\text{a})}$	1382–1386	1384–1387
$\tau(\text{CH}_2)$ in DOM	1301–1303	1293–1299
$\omega(\text{CH}_2)$ in $\text{H}_2\text{CO}_{(\text{a})}$	1251–1253	1251
$\rho(\text{CH}_2)$ in $\text{H}_2\text{CO}_{(\text{a})}$	1134–1170	1155–1164
$\rho(\text{CH}_2)$ in DOM	1116	1112
$\nu(\text{CO})$ in DOM	1064–1067	1058–1064
$\nu(\text{CO})$ in POM	963, 936	967–953

TiO<sub>2</sub>. The coupling of CH<sub>2(a)</sub> species may result in C<sub>2</sub>H<sub>4</sub>. The dehydrogenation of a part of CH<sub>2(a)</sub> can produce CH<sub>(a)</sub>, the coupling of which leads to the appearance of C<sub>2</sub>H<sub>2</sub> in the gas phase.

Some of the oxygen vacancies produced during the pre-treatments could be blocked by metal crystallites on Pt/TiO<sub>2</sub> and Au/TiO<sub>2</sub> [39]. This would reduce the probability of the formation of CH<sub>2(a)</sub> and CH<sub>(a)</sub>, thus the production of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> was hindered on Pt/TiO<sub>2</sub> and Au/TiO<sub>2</sub> catalysts. Formic acid may form in the interaction of formaldehyde with the surface OH groups of titania. Most of HCOOH thus formed desorbs from the oxidized TiO<sub>2</sub>, on reduced TiO<sub>2</sub>, however, due to the higher surface concentration of oxygen vacancies, a part of HCOOH decomposes depending on the reaction temperature. When metal was present on the TiO<sub>2</sub> surface formic acid decomposes very quickly on the metal sites, this may explain why formic acid was not detected in the gas phase during the interaction of formaldehyde with metal/TiO<sub>2</sub> catalysts.

## 5. Conclusions

1. Molecularly adsorbed formaldehyde, formic acid, formate, dioxymethylene (DOM) and polyoxymethylene surface species formed during the interaction of formaldehyde with Pt/TiO<sub>2</sub> and Au/TiO<sub>2</sub> catalysts.
2. Decomposition of molecularly adsorbed H<sub>2</sub>CO and DOM resulted in mainly H<sub>2</sub> and CO in the gas phase.
3. Ethylene, acetylene and formic acid appeared in the gas phase in the reaction of formaldehyde and pure TiO<sub>2</sub>.
4. No ethylene, acetylene and formic acid was detected on metal-containing TiO<sub>2</sub> catalysts.
5. These data may confirm the former suggestion that the main source of CO in the catalytic transformation of HCOOH can be the thermal decomposition of formaldehyde produced by the deoxygenation of HCOOH.

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