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Adsorption and reaction of formaldehyde on TiO_2-supported Rh catalysts studied by FTIR and mass spectrometry

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Abstract

The adsorption and surface reactions of formaldehyde were studied on TiO_2 and Rh/TiO_2 catalysts at 300–473 K by Fourier-transform infrared spectroscopy (FTIR) and mass spectrometry (MS). FTIR bands due to molecularly adsorbed formaldehyde, formate, and formic acid were detected. The dominant surface species was dioxymethylene (DOM, $H_2CO_{2(a)}$) species, a part of which underwent surface polymerization resulting in polyoxymethylene (POM) on the surface. At higher temperatures molecularly adsorbed formaldehyde and DOM surface species decompose producing mainly H_2 and CO in the gas phase. The amounts of H_2 and CO were proportional with the Rh content of the catalysts. The quantity of ethylene (also formed in the above decomposition), however, changed inversely with the increase of Rh content.

Keywords: Formaldehyde adsorption and reaction; TiO_2 and Rh/TiO_2 catalysts; FTIR; MS

1. Introduction

Formaldehyde seems to be one of the most important compounds in organic catalytic reactions. To illustrate this statement only some samples are noted: it is either the product [1] or an intermediate [2] in methanol oxidation, and it is thought to be the key intermediate in methanol dehydrogenation [3], in methanol synthesis [4], in the catalytic production of higher alcohols [5] and in Fischer–Tropsch synthesis [6].

The adsorption and reaction of formaldehyde have been studied on single crystal surfaces of metal oxides [7–11] and on several metal oxide powders [12–14]. It has been generally accepted that the reactions of formaldehyde on these surfaces include both its oxidation (producing surface formate, $HCOO_{(a)}$) and its Cannizaro-type disproportionation (resulting in the formations of surface formate ($HCOO_{(a)}$) and methoxide, ($CH_3O_{(a)}$); both likely involve the formation of dioxymethylene species ($H_2COO_{(a)}$) by nucleophilic attack of surface oxygen atoms at the carbonyl carbon.

Studies of formaldehyde adsorption on metal single crystal surfaces [13,15–17] revealed two different molecular adsorption states: η^2(C,O) and η^1(O) formaldehyde. Evidence for oxidation of η^1-formaldehyde to surface formates has been obtained on a variety of oxygen-containing metal surfaces [18–23].

The investigations of formaldehyde adsorption on powdered TiO_2 led to different results and conclusions. It has been shown [24] that formaldehyde is oxidized to surface formate species on rutile at 373 K and that the formate species decompose back to formaldehyde below 573 K. It was reported [25] that formaldehyde reacts on titania at 550 K to produce methyl formate via the Tischenko reaction, while the formation of dioxymethylene, formate, and methoxide species was observed [26] following the adsorption of formaldehyde on titania (anatase) at 300 K. It has been also reported [12] that at 200–250 K dioxymethylene is predominant in a mixture with polyoxymethylene (paraformaldehyde), and is converted to methoxide and formate species via the Cannizaro reaction at room temperature. From the studies on the reaction of formaldehyde on TiO_2(001) single crystal surfaces [27] it has been concluded that the oxidation state of surface cations plays a decisive role in the formation of different surface species and gas-phase products.

Recently it has been found that formaldehyde forms both in the adsorbed layer and in the gas phase during the interaction of formic acid with TiO_2-supported noble metal

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catalysts [28,29], and its decomposition would be the main source of CO formation in the catalytic reaction of formic acid.

The later findings motivated the present study of formaldehyde interaction with TiO_2-supported rhodium catalysts.

2. Experimental

TiO_2 was the product of Degussa (P25, 50 m^2/g). 1 and 5 wt% Rh/TiO_2 catalysts were prepared by impregnating TiO_2 with an aqueous solution of $RhCl_3 \times 3H_2O$ (Johnson Matthey). The impregnated powders were dried at 383 K for 3 h. Formaldehyde was prepared by the thermal decomposition of paraformaldehyde (Reanal) at 453–473 K.

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): (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 dispersions of Rh were determined via H_2 adsorption at 298 K with the use of a dynamic impulse method [30]: the dispersion of reduced 1% Rh/TiO_2 was 30% [31] and that of 5% Rh/TiO_2 was 27%. The average particle sizes were calculated on the basis of dispersity data [32,33]: the average particle size of Rh was 2.88 nm on 1% Rh/TiO_2, 3.2 nm on 5% Rh/TiO_2.

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 CO_2- and H_2O-free air generated by a Balston 75-62 FTIR purge gas generator. Experiments were performed in a batch mode. The spectrum of the pretreated sample (background spectrum) and the actual vapor spectrum were subtracted from the spectrum registered in the presence of vapor. 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 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 the intensity ratio 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.

3. Results

3.1. Infrared spectroscopic studies

First the development of different IR bands on the spectra of oxidized TiO_2 was followed as a function of formaldehyde pressure at 300 K. In 0.01 Torr of CH_2O bands at 2967, 2922, and 2865 cm^{-1} appeared in the C–H stretching region; below 2200 cm^{-1} bands at 1589, 1539, 1454, 1379, 1303, 1253, 1115, 1062, and 946 cm^{-1} were detected (Fig. 1). With the increase of formaldehyde pressure a new band at 2755 cm^{-1} appeared in the range of 3100–2600 cm^{-1} and the intensities of the bands at 2922 and 2865 cm^{-1} increased more than the 2967 cm^{-1} band. In the lower wavenumber region new bands at 1713, 1663, 1551, 1409, and 1149 cm^{-1} were detected; the later shifted to 1162 cm^{-1} at the highest formaldehyde pressure applied (1 Torr).

The adsorption of 1 Torr formaldehyde on oxidized TiO_2 at different temperatures caused dramatic changes in the IR spectra in comparison with that registered at 300 K. In the C–H stretching region the 2755 cm^{-1} band disappeared at 383 K. The position of the 2866 cm^{-1} band remained constant; its intensity, however, decreased with increasing adsorption temperature. The band at 2967 cm^{-1} shifted slightly to lower wavenumbers with concomitant decrease of its intensity. The intensity of the 2912 cm^{-1} band diminished only a small extent with the increase of the adsorption temperature. Below 2200 cm^{-1} bands at 1411, 1303, 1252, 1166, and 946 cm^{-1} disappeared, while the bands at 1113 and 1062 cm^{-1} (registered at 300 K) shifted to 1125 and 1047 cm^{-1} at higher adsorption temperatures (Fig. 2). The reduction of TiO_2 basically did not modify the spectral features obtained on oxidized surfaces (Fig. 4).

The presence of rhodium (1%) on TiO_2 caused significant changes on the IR spectra. In the C–H stretching region the bands at 2980, 2917, 2870, 2815, 2766, and 2724 cm^{-1} were detected in the adsorption of 0.01 Torr of formaldehyde at 300 K on oxidized 1% Rh/TiO_2 (Fig. 3). We note that among these absorptions only three bands (2922, 2865, and 2755 cm^{-1}) appeared on the spectrum of TiO_2. In the range of 1800–900 cm^{-1} the spectral features of 1% Rh/TiO_2 were very similar to those observed on TiO_2, above 1800 cm^{-1}, however, bands at 2043 and 2001 cm^{-1} due to CO adsorbed on Rh sites appeared on the spectrum of 1% Rh/TiO_2. With the increase of the formaldehyde pressure the intensities of the bands appeared in the ranges of 3100–2600 and 1800–900 cm^{-1} increased. The band detected at 2980 cm^{-1} in

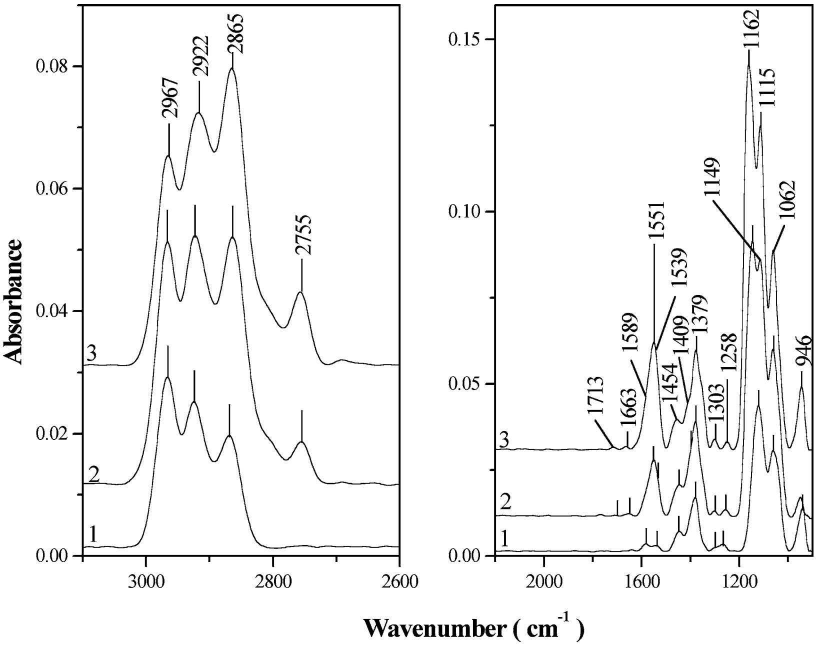

Fig. 1. IR spectra registered at 300 K on oxidized TiO_2 during the adsorption of formaldehyde at different pressures (adsorption time 1 min): 1, 0.01 Torr; 2, 0.1 Torr; and 3, 1 Torr.

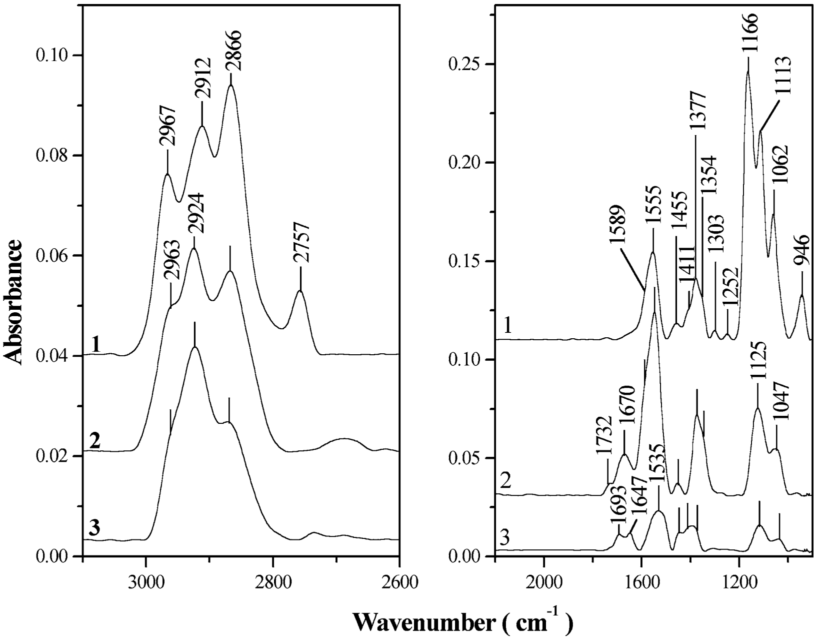

Fig. 2. IR spectra of 1 Torr formaldehyde adsorbed on oxidized TiO_2 at different temperatures for 60 min: 1, 300 K; 2, 383 K; and 3, 473 K. (The spectra were taken at the adsorption temperatures.)

0.01 Torr formaldehyde shifted to lower wavenumbers with the increase of formaldehyde pressure. New band appeared at 1155 cm^{-1} in 0.1 Torr and at 1166 cm^{-1} in 1 Torr of formaldehyde.

The intensities of the bands due to adsorbed CO also increased with increasing formaldehyde pressure. Interestingly, besides the 2043 and 2001 cm^{-1} bands new bands at 2094 and 2150 cm^{-1} were detected in 0.1 Torr formaldehyde, which shifted (with higher intensities) to 2082 and 2157 cm^{-1} in 1 Torr.

After the reduction of 1% Rh/TiO_2 significantly smaller bands due to adsorbed species formed during the formaldehyde adsorption were detected in comparison with that observed on oxidized surface (Fig. 4). The band that appeared at 2980 cm^{-1} on the oxidized surface was not observable on the reduced 1% Rh/TiO_2 in 0.01 Torr formaldehyde. In 0.1 Torr a band at 2963 cm^{-1} was detected, which shifted to 2968 cm^{-1} with the further increase of formaldehyde pressure to 1 Torr. Note that an opposite shift (from 2980 to 2966 cm^{-1}) was observed on oxidized 1% Rh/TiO_2.

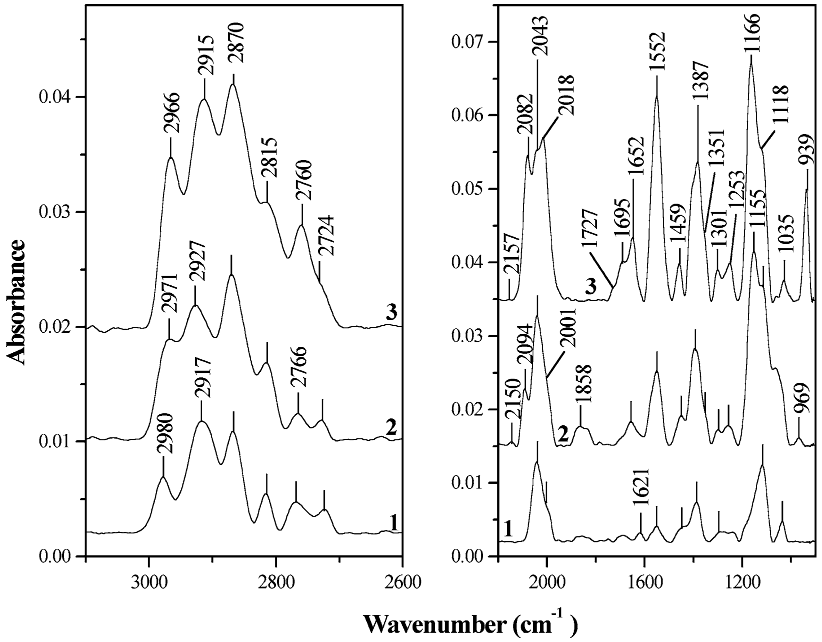

Fig. 3. IR spectra registered at 300 K on oxidized 1% Rh/TiO$_2$ during the adsorption of formaldehyde at different pressures (adsorption time 1 min): 1, 0.01 Torr; 2, 0.1 Torr; and 3, 1 Torr.

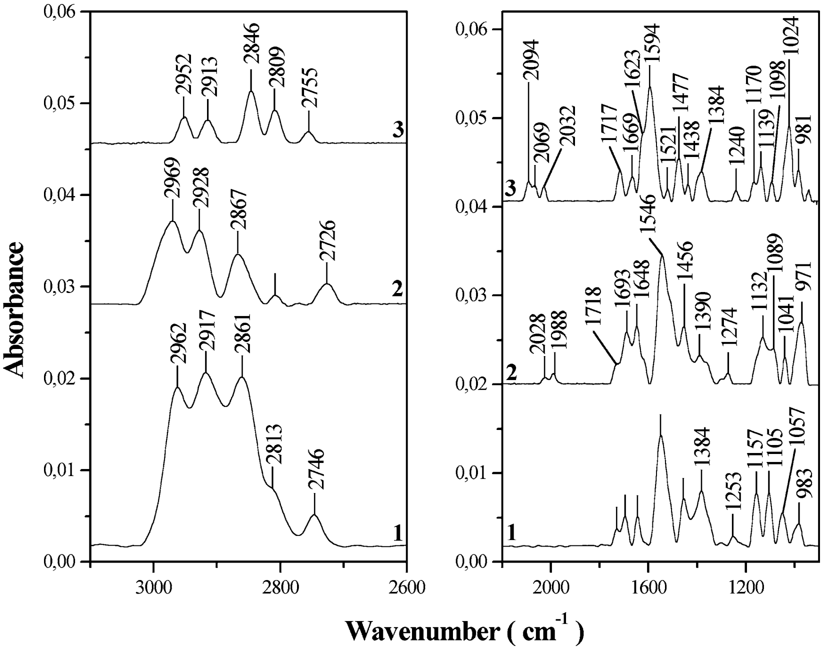

Fig. 4. IR spectra registered in 1 Torr formaldehyde at 300 K (adsorption time = 15 min) on: 1, reduced TiO$_2$; 2, reduced 1% Rh/TiO$_2$; and 3, reduced 5% Rh/TiO$_2$.

The intensities of the bands due to surface species formed on oxidized 1% Rh/TiO$_2$ decreased with the increase of adsorption temperature (Fig. 5). The band observed at 2969 cm^{-1} at 300 K shifted to 2977 cm^{-1} and a new band at 2731 cm^{-1} appeared at higher temperatures. The most obvious changes occurred in the range of 2200–1800 cm^{-1}. Among the bands due to different forms of adsorbed CO (2157, 2082, 2043, 2014, and 1849 cm^{-1}) registered at 300 K, only the bands at 2140, 2023, and 1849 cm^{-1} remained during the adsorption at 383 K. At 473 K only one band at 2070 cm^{-1} appeared in this range. At 383–473 K the 1717 cm^{-1} band could be clearly distinguished.

The same type of experiments on reduced 1% Rh/TiO$_2$ led to the appearance of similar bands with significantly smaller intensities. In contrast with the results obtained on oxidized surface, relatively intense bands at 1693 and 1648 cm^{-1} were detected on reduced 1% Rh/TiO$_2$ at 300–473 K.

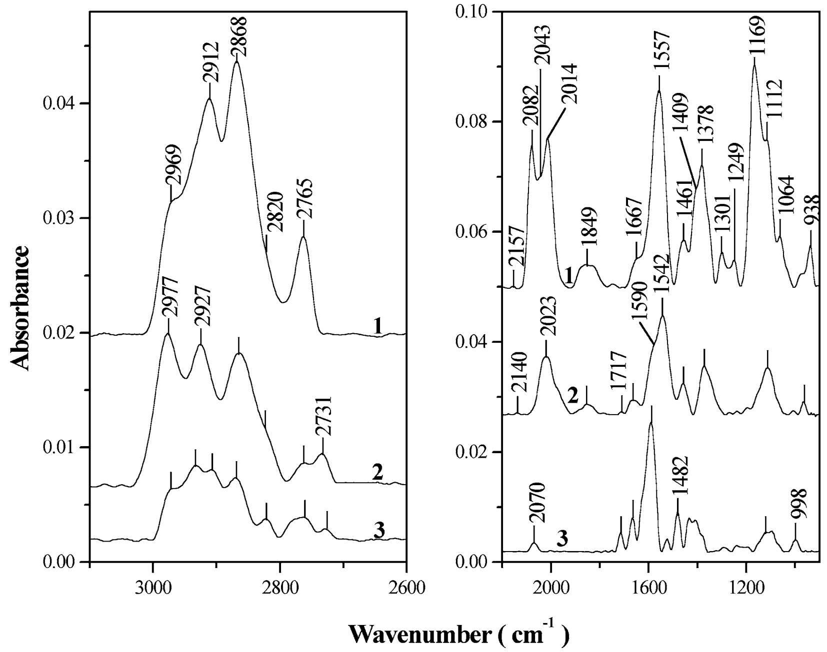

Fig. 5. IR spectra of 1 Torr formaldehyde adsorbed on oxidized 1% Rh/TiO$_2$ at different temperatures for 60 min: 1, 300 K; 2, 383 K; and 3, 473 K. (The spectra were taken at the adsorption temperatures.)

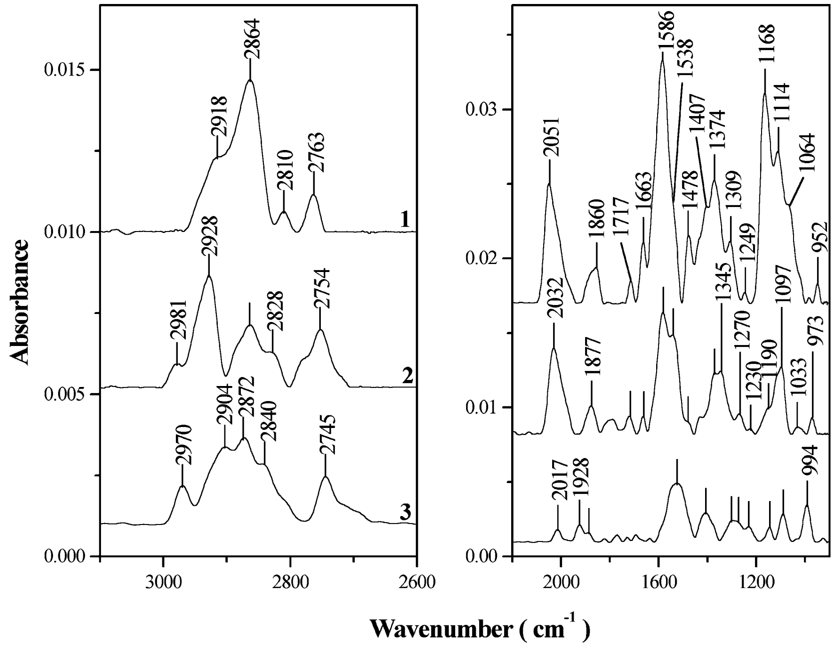

Fig. 6. IR spectra of 1 Torr formaldehyde adsorbed on oxidized 5% Rh/TiO$_2$ at different temperatures for 60 min: 1, 300 K; 2, 383 K; and 3, 473 K. (The spectra were taken at the adsorption temperatures.)

The increase of rhodium content to 5 wt% caused a significant decrease in the intensities of the bands. On Fig. 6 we collected the spectra taken at different temperatures after the adsorption of formaldehyde (1 Torr) for 60 min on oxidized 5% Rh/TiO$_2$. These spectra show qualitatively similar features as observed on oxidized 1% Rh/TiO$_2$ (Fig. 5), there are, however, some differences that might be due to the higher Rh content. The 2810 cm^{-1} band, which appeared at 300 K, shifted to higher wavenumbers, while the 2763 cm^{-1} band shifted to lower wavenumbers with the increase of the adsorption temperature on 5% Rh/TiO$_2$. Another obvious difference is that only one band at 2051 cm^{-1} can be observed above 2000 cm^{-1} on the spectra of 5% Rh/TiO$_2$; the position of this band shifted to lower wavenumbers when the adsorption temperature was higher.

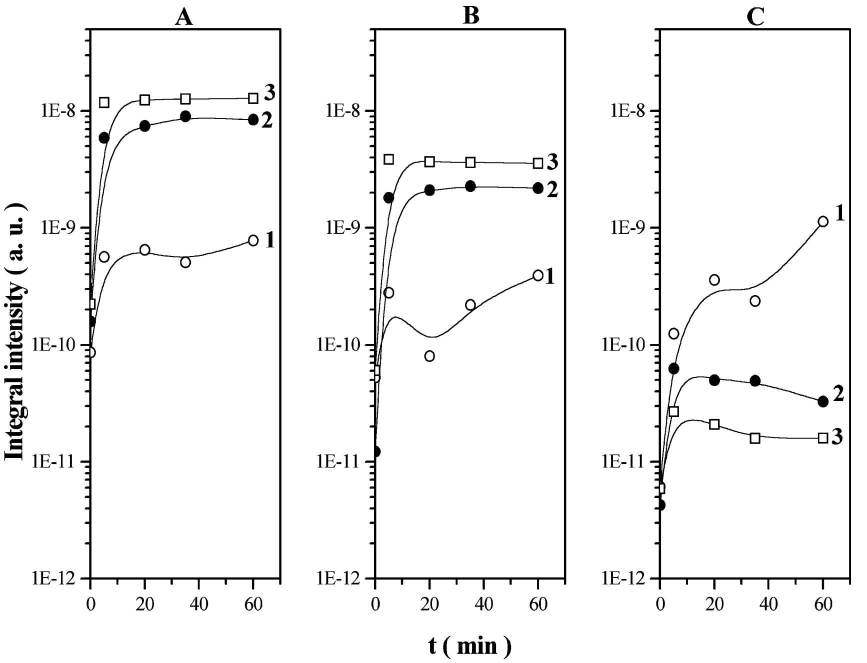

Fig. 7. Formation of H_2 (A), CO (B), and C_2H_4 (C) in the gas phase (detected by mass spectrometer) during the reaction of 1 Torr formaldehyde with reduced catalysts at 473 K: 1, TiO_2; 2, 1% Rh/TiO_2; and 3, 5% Rh/TiO_2.

3.2. Mass spectrometric investigations

Parallel with the FTIR studies the changes in the gas-phase composition were monitored by a mass spectrometric method.

The main gas-phase products in the interaction of formaldehyde and the catalysts investigated were hydrogen and carbon monoxide. The pretreatments and the rhodium content of the catalysts did not influence the amounts of H_2 and CO at 300 K. At higher temperatures, however, the formation of H_2 and CO was clearly dependent on the rhodium content (Figs. 7A and B): it was found that the higher the rhodium content, the higher the amounts of H_2 and CO. Interestingly, at 383–473 K the catalysts' pretreatment did not affect the amounts of hydrogen and CO.

The formation of ethylene was also detected by MS on reduced surfaces at all temperatures. Among the oxidized surfaces only oxidized TiO_2 was to be active in C_2H_4 production at 473 K. The amount of ethylene was dependent on the rhodium content of the catalysts: the higher the Rh content, the smaller the amount of C_2H_4 formed (Fig. 7C).

On reduced surfaces the formation of formic acid (HCOOH) and acetylene (C_2H_2) was experienced. Their amounts depended on the reaction temperature and on the Rh content of the catalysts. HCOOH and C_2H_2 were produced in the greatest amount at 300 K (Fig. 8), their amounts decreased with the increase of the reaction temperature. Practically no HCOOH and C_2H_2 formation was observed on reduced 5% Rh/TiO_2 at any temperatures. Reduced 1% Rh/TiO_2 was more active in producing HCOOH and C_2H_2 than reduced TiO_2. There was no HCOOH and C_2H_2 formation on oxidized 1 and 5% Rh/TiO_2 at 300–473 K and on oxidized TiO_2 at 300–383 K. These products, however, appeared in the gas phase in the interaction of formaldehyde with oxidized TiO_2 at 473 K.

The signal of H_2CO was decreased with the increase of the signals due to the products. The disappearance of the signal due to H_2CO depended on the reaction temperature, on the metal content of the catalysts, and on the pretreatment of the catalysts.

4. Discussion

For convincing assignments of the bands detected in the present study, literature data on formaldehyde molecular species in the gas phase [34,35], in solid [36], in the condensed phase [37], and in the adsorbed layer on oxide [12] have been collected and presented in Table 1. Molecular adsorption of formaldehyde occurs through σ lone pair donation from the oxygen of carbonyl to Lewis acid sites (in the present case Ti^{4+} surface cations) [41]. As a result of this adsorption the carbon of the carbonyl becomes more electrophilic, favoring an attack from a nucleophilic surface oxygen ions to form dioxymethylene (DOM, $H_2CO_{2(a)}$) species [27]. Characteristic bands of dioxymethylene are shown in Table 2. Dioxymethylene species have been observed following formaldehyde adsorption on TiO_2, as well as on ZrO_2 and on ThO_2 [12]. Surface polymerization of dioxymethylene resulting in the formation of polyoxymethylene (POM) on ZrO_2, ThO_2, TiO_2, and MgO has been experienced [12]. Bands due to polyoxymethylene are also presented in Table 2.

Hydride transfer between two dioxymethylene species would give one methoxide ($CH_3O_{(a)}$) and one formate

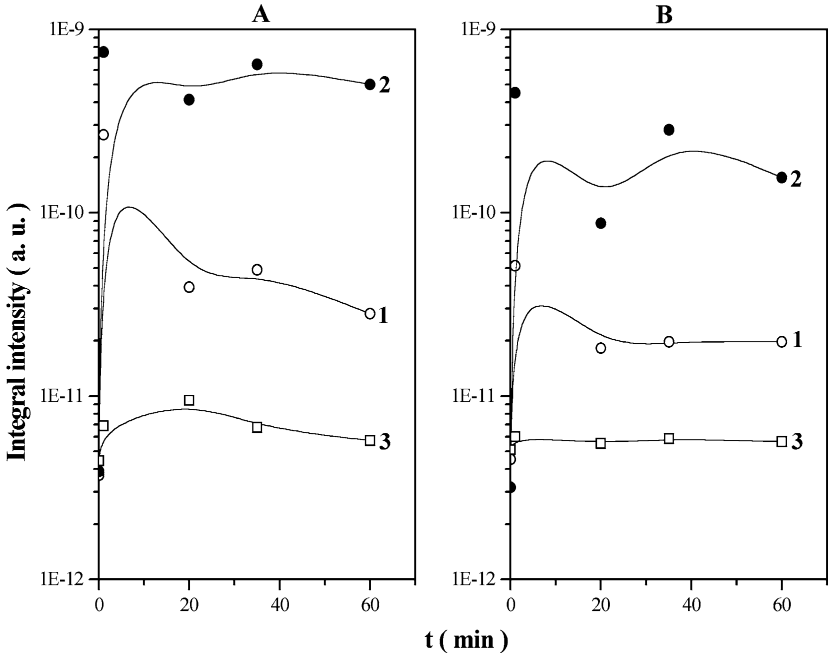

Fig. 8. Formation of gas-phase HCOOH (A) and C_2H_2 (B) (detected by mass spectrometer) in the reaction of 1 Torr formaldehyde with reduced catalysts at 300 K: 1, TiO_2; 2, −1% Rh/TiO_2; and 3, 5% Rh/TiO_2.

Table 1
Observed wavenumbers (cm^{-1}) of formaldehyde molecular species

Assignment	Gas [34,35]	Solid monomer [36]	Condensed on Ag [37]	On Al_2O_3 at 170 K [12]
$\nu_{as}(CH_2)$	2843.3	2843	2850	2885
$\nu_s(CH_2)$	2782.5	2783	nr	2818
$\delta(CH_2) + \omega(CH_2)$	2719.2			2725
$\nu(CO)$	1746.1	1746	1710	1718
$\delta(CH_2)$	1500.1	1500	1490	1498, 1485
$\omega(CH_2)$	1249.3	1249/1167	1250	1252
$\gamma(CH_2)$	1167.1			

($HCOO_{(a)}$). This reaction corresponds to a net Cannizaro disproportionation. Both the formations of methoxide and formate have been detected on powdered oxides [12,42] and on TiO_2(001) surfaces [27] at relatively moderate temperatures [270–300 K]. At a higher temperature (∼ 410 K) the formation of methylformate ($HCOOCH_3$) was also supposed [42], through the reaction of two molecularly adsorbed formaldehyde species.

All these findings pointed out that although HCHO is a relatively simple molecule its adsorption and surface transformations are very complex.

Taking into account the literature assignments, bands due to the formation of molecularly adsorbed formaldehyde (2815, 2724, 1713–1727, 1253, and 1149–1166 cm^{-1}), formate (2963–2970, 1551–1552, and 1379–1387 cm^{-1}), formic acid (1695 cm^{-1}), dioxymethylene (2865–2870, 2755–2766, 1454–1459, 1409–1411, 1301–1303, 1115–1118, and 1035–1062 cm^{-1}), and polyoxymethylene (2917–2922 and 936–969 cm^{-1}) were detected in the present study.

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

DOM		POM	
Assignment	In $H_2C(OCD_3)_2$ [38,39]	Assignment	Hexagonal POM [40]
		$\nu(CH_2)$	2984
			2920
$\nu_{as}(CH_2)$	2945		
$2\delta(CH_2)$	2932		
$\nu_s(CH_2)$	2882		
$2\omega(CH_2)$	2770		
$\delta(CH_2)$	1473	$\delta(CH_2)$	1471
			1384
$\tau(CH_2)$	1302	$\tau(CH_2)$	1290
$\rho(CH_2)$	1186	$\rho(CH_2)$	1238
ν(C–O)	1138	ν(C–O)	1098
	1114		936
	1086		897
	858		

No bands due to methoxide and methylformate were observed (Table 3).

The dominant surface species formed at 300 K in formaldehyde adsorption on TiO_2 proved to be dioxymethylene. Its surface concentration together with that of molecularly adsorbed formaldehyde, however, significantly decreased with the increase of the adsorption temperature, possibly due to the surface reactions resulting in the formation of gas-phase products. Polyoxymethylene species were somewhat more stable. 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

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

Assignment	$\mathrm{TiO_2}$	$\mathrm{Rh/TiO_2}$
$\nu(\mathrm{OCO}) + \delta(\mathrm{CH})$ in $\mathrm{HCOO_{(a)}}$	2967	2963–2970
$\nu(\mathrm{CH_2})$ in POM	2922	2917
$\nu_s(\mathrm{CH_2})$ in DOM	2865	2870
$\nu_s(\mathrm{CH_2})$ in $\mathrm{H_2CO_{(a)}}$		2815
$2\omega(\mathrm{CH_2})$ in DOM	2755	2766
$\delta(\mathrm{CH_2}) + \omega(\mathrm{CH_2})$ in $\mathrm{H_2CO_{(a)}}$		2724
$\nu(\mathrm{CO})$ in $\mathrm{H_2CO_{(a)}}$	1713	1727
$\nu(\mathrm{CO})$ in $\mathrm{HCOOH_{(a)}}$	1663	1695
$\nu_a(\mathrm{OCO})$ in $\mathrm{HCOO_{(a)}}$	1551	1552
$\delta(\mathrm{CH_2})$ in DOM	1454	1459
$\omega(\mathrm{CH_2})$ in DOM	1409–1411	
$\nu_s(\mathrm{OCO})$ in $\mathrm{HCOO_{(a)}}$	1379	1387
$\tau(\mathrm{CH_2})$ in DOM	1303	1301
$\omega(\mathrm{CH_2})$ in $\mathrm{H_2CO_{(a)}}$	1253	1253
$\rho(\mathrm{CH_2})$ in $\mathrm{H_2CO_{(a)}}$	1149–1162	1166
$\rho(\mathrm{CH_2})$ in DOM	1115	1118
$\nu(\mathrm{CO})$ in DOM	1062	1035
$\nu(\mathrm{CO})$ in POM	946	969–936

could lead to the formation of formic acid, the dissociation of which may also cause the appearance of surface formate, and surface hydroxyl group.

The presence of rhodium on titania surface enhances the possibility of the formaldehyde decomposition into H_2 and CO. This manifested in the less intense DOM and POM bands and in the appearance of the bands due to CO adsorbed on metal sites in the cases of $\mathrm{Rh/TiO_2}$ catalysts. In the gas phase, on the other hand, the quantities of H_2 and CO increased with the increase of the rhodium content of the catalysts. This observation strengthens further the decisive role of Rh in the decomposition of formaldehyde.

The bands due to adsorbed CO characterize the actual surface structure and oxidation state of the metal. CO bands appearing on oxidized 1% $\mathrm{Rh/TiO_2}$ are connected with CO adsorbed on highly oxidized Rh cations ($\mathrm{Rh^{3+}}$–CO, 2150–2157 $\mathrm{cm^{-1}}$), with twin CO on $\mathrm{Rh^+}$ of two-dimensional Rh rafts ($\mathrm{Rh^+(CO)_2}$, 2094–2082 and 2001 $\mathrm{cm^{-1}}$), and with CO adsorbed on $\mathrm{Rh^0}$ surrounded by only $\mathrm{Rh^0}$ atoms ($\mathrm{Rh^0}$–CO, 2043 $\mathrm{cm^{-1}}$) [43]. At 473 K only the 2070 $\mathrm{cm^{-1}}$ band (due to CO adsorbed on $\mathrm{Rh^0}$ surrounded by only $\mathrm{Rh^0}$ atoms) appeared, which shows that at this temperature a reductive agglomeration of Rh rafts occurred during the interaction of formaldehyde with the oxidized 1% $\mathrm{Rh/TiO_2}$.

On 5% $\mathrm{Rh/TiO_2}$ (even on oxidized catalyst) only the 2051 $\mathrm{cm^{-1}}$ band due to CO adsorbed on $\mathrm{Rh^0}$ appeared at 300–473 K. This can be accepted as a proof that even the oxidation (at 573 K) of 5% $\mathrm{Rh/TiO_2}$ led to the formation of three-dimensional Rh crystallites with relatively large particle size, which provides $\mathrm{Rh^0}$ surrounded by only Rh atoms.

All these observations permit the conclusion that the decomposition of formaldehyde should be a net reductive process; no oxidation of the catalyst surfaces could be observed during this reaction.

Another interesting result was the detection of ethylene in the gas phase. We note here that ethylene formation on defected $\mathrm{TiO_2}$ surfaces was interpreted [44–47] as a result of the reductive coupling of two molecules of formaldehyde. As an alternative explanation for $\mathrm{C_2H_4}$ formation we suppose the adsorption of formaldehyde with its O end at the oxygen vacancies and the consecutive breaking of the C–O bond. These processes would result in the formation of $\mathrm{CH_{2(a)}}$, the coupling of which may also lead to the ethylene production.

The formation of gas-phase ethylene depended inversely on the rhodium content of the reduced catalysts. It can be supposed that this feature can be connected with the surface concentration of oxygen vacancies on titania. Some of the oxygen vacancies produced during the preliminary reduction at 573 K could be blocked by Rh crystallites on $\mathrm{Rh/TiO_2}$ catalysts [48], thus the probability of the formation of $\mathrm{CH_{2(a)}}$ diminished with the increase of Rh content, and as a consequence, rather the decomposition of formaldehyde into H_2 and CO on the metal sites came into prominence.

The formation of acetylene ($\mathrm{C_2H_2}$) on reduced $\mathrm{TiO_2}$ and 1% $\mathrm{Rh/TiO_2}$ may be the result of $\mathrm{CH_{(a)}}$ coupling; $\mathrm{CH_{(a)}}$ could be produced in the dehydrogenation of $\mathrm{CH_{2(a)}}$ formed on the oxygen vacancies of titania. The importance of the oxygen vacancies in the formation of acetylene is reflected in the fact that in the absence of them (on oxidized surfaces and on reduced 5% $\mathrm{Rh/TiO_2}$—see above) no acetylene was detected among the gas-phase products. In the interaction of formaldehyde with oxidized $\mathrm{TiO_2}$ at 473 K, however, oxygen vacancies can be formed due to the high temperature and the reductive atmosphere, consequently acetylene appeared in the gas phase.

All the above data confirm the former suggestion [28,29] that the decomposition of formaldehyde formed during HCOOH adsorption is the main source of the CO formation in the catalytic reaction of HCOOH.

5. Conclusions

1. Formaldehyde adsorption led to the formation of molecularly adsorbed $\mathrm{H_2CO}$, formate, formic acid, dioxymethylene, and polyoxymethylene on $\mathrm{TiO_2}$ and $\mathrm{Rh/TiO_2}$ catalysts at 300 K.
2. At higher temperatures the surface concentrations of molecularly adsorbed $\mathrm{H_2CO}$ and DOM significantly decreased possibly due to their decomposition mainly into gas-phase H_2 and CO.
3. The active sites of formaldehyde decomposition resulting in H_2 and CO are surface Rh atoms.
4. The production of ethylene might be connected with the oxygen vacancies on $\mathrm{TiO_2}$.
5. The data presented confirm that CO formed in the HCOOH catalytic reaction mainly through formaldehyde decomposition.

Acknowledgments

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