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FT-IR and mass spectrometric studies on the interaction of acetaldehyde with TiO_2-supported noble metal catalysts

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Abstract

Surface species formed during the adsorption of acetaldehyde at 300–673 K on TiO_2-supported Pt, Rh and Au catalysts were investigated by Fourier transform infrared spectroscopy. Two forms of molecularly adsorbed acetaldehyde–H-bridge bonded on surface OH groups and adsorbed on Lewis sites through one of the oxygen lone pairs–were identified. β-aldolization of acetaldehyde led to the formation of crotonaldehyde, which adsorbs on Lewis sites of TiO_2 through one of the oxygen lone pairs and on metallic sites via the C atom of the aldehyde group. Adsorbed acetaldehyde can be oxidized into surface acetate and it can be reduced resulting in adsorbed ethoxy. Mass spectroscopic analysis of the gas phase composition revealed that the formation of gas phase products (crotonaldehyde, water, benzene, hydrogen, ethylene, acetylene and methane) depends on the nature of the metals and the reaction temperature. An attempt was made to find a possible link between the surface species and the formation of the primary gas phase products.

Keywords: Acetaldehyde adsorption; TiO_2-supported Pt; Rh; Au catalysts; Surface species; Gas phase products; FT-IR; MS

1. Introduction

The number of publications on the steam reforming of ethanol producing H_2-rich (CO-free) gas mixture has recently grown exponentially [1–12]. This is connected with the demand for alternative sources of energy. The application of H_2 in fuel cells or in electric vehicles ensures the cleanest source of electric energy with practically zero emission of polluting gases. From an environmental point of view the use of ethanol + water mixture as hydrogen source is preferred because it can be readily produced from renewable biomass.

It has recently been found [13] that acetaldehyde is an important surface and gas phase product in the catalytic steam reforming of ethanol. Its appearance either in the adsorbed layer, or in the gas phase has been regarded as an indication of H_2 production. If H_2 were catalytically produced from ethanol (+water mixture) in the vehicles, the presence of acetaldehyde in the exhaust would represent high danger to the environment because of its potential carcinogen effects [14]. Thus, its catalytic transformation to less dangerous materials would play a vital role.

There are only few papers dealing with the interaction between acetaldehyde and oxide-supported transitional metals [15,16].

In this work we intended to perform a detailed and systematic study of the adsorption and further surface reactions of acetaldehyde on TiO_2-supported noble metals (Pt, Rh and Au). Among these catalysts Rh/TiO_2 proved to be active and effective in the steam reforming of ethanol [17]. Pt/TiO_2 and Au/TiO_2 catalysts are potentially good catalysts for this reaction. Thus, the study on the reactions of acetaldehyde on these catalysts has special aspects, too.

2. Experimental

TiO_2 was the product of Degussa (P25, 50 m^2/g). 1% Pt/TiO_2 and 1% Rh/TiO_2 catalysts were prepared by

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impregnating of TiO_2 with an aqueous solution of $H_2PtCl_6{\cdot}3H_2O$ (Reanal) and with that of $RhCl_3{\cdot}3H_2O$ (Johnson Matthey), respectively. The impregnated powders were dried at 383 K for 3 h. TiO_2 supported Au catalyst was made by a deposition–precipitation method. Chloroauric acid ($HAuCl_4{\cdot}aq$ p.a. 49% Au, Fluka AG) was first dissolved 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 the supporting oxide 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.

Acetaldehyde was of 99.8% purity (Riedel de Haen) 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 × 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 1.33×10^{-5} Pa): the samples were heated in 1.33 hPa of H_2 up to 573 K and it was kept at this temperature for 1 h. This was followed by degassing at the same temperature for 30 min and by cooling the sample to the temperature of the experiment.

The dispersion of the reduced 1% Pt/TiO_2 was 29% determined by H_2 adsorption at room temperature. The dispersion of Rh were determined via H_2 adsorption at 298 K with the use of a dynamic impulse method [18]: the dispersion of reduced 1% Rh/TiO_2 was 30%. The dispersion of Au was measured by CO adsorption following the method suggested by Shastri et al. [19]. The dispersion of Au was relatively high (46%) for 1% Au/TiO_2 [20]. The average particle sizes were calculated on the basis of dispersion data [21,22]: the average particle size of Pt on 1% Pt/TiO_2 was 3.1 nm, that of Rh was 2.88 nm on 1% Rh/TiO_2, and that of Au was 1.96 nm on 1% Au/TiO_2.

Infrared spectra were recorded with a Genesis (Mattson) FT-IR 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 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 6.65×10^{-4} Pa around the MS head when reacting gases were present in the cell. The changes in the signal intensity of the main fragments of acetaldehyde 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 and discussion

The infrared bands due to molecularly adsorbed acetaldehyde(I) (ν_{as} (CH_3) at 2965 cm^{-1}, ν_s (CH_3) at 2924 cm^{-1}, ν (CH) at 2730 cm^{-1}, ν (C=O) at 1722–1685 cm^{-1}, δ_{as} (CH_3) at 1442 cm^{-1}, δ (CH) at 1376 cm^{-1}, δ_s (CH_3) at 1338 cm^{-1} and γ (CH_3), ν (C–C) at 1120 cm^{-1}), due to adsorbed crotonaldehyde(II) (ν (C=O) at 1645–1629 cm^{-1}, ν (C=C) at 1594 cm^{-1}, δ (C–H) at 1259 cm^{-1}, ν (CC) at 1167 cm^{-1} and ρ (CH_3) at 975 cm^{-1}), due to surface acetate(III) (ν_{as} (COO) at 1526 cm^{-1}) and due to ethoxy(IV) (ν_s (CH) at 2867 cm^{-1} and ν (CO) at 1075 cm^{-1}) appeared already in 1.33 Pa acetaldehyde at 300 K on reduced catalysts. With the increase of acetaldehyde pressure the intensities of the above bands increased. Spectra registered in 1.33 hPa acetaldehyde have been collected in Fig. 1.

As concerns the coordination modes of acetaldehyde on the surfaces of the catalysts, the relevant shift down of the acetaldehyde C=O stretching (from 1730 to 1722–1685 cm^{-1}) suggests that a part of acetaldehyde is adsorbed on Lewis sites through one of the oxygen lone pairs. Spectroscopic features observed above 3400 cm^{-1} revealed another coordination mode of acetaldehyde: the negative features at 3698 cm^{-1} and at 3641 cm^{-1} as well as broad absorptions (centered at 3536 cm^{-1} in 1.33 hPa acetaldehyde on TiO_2, at 3484 cm^{-1} in 13.3–1.33 hPa acetaldehyde on Pt/TiO_2 and at 3448 cm^{-1} in 1.33 hPa acetaldehyde on Au/TiO_2) show that another part of acetaldehyde may adsorb through H-bridge bonding with OH groups of these surfaces. No spectroscopic evidences for H-bridge bonding were registered on Rh/TiO_2.

Based on the bands appearing on the spectra it can be concluded that acetaldehyde undergoes different surface reactions already at 300 K: (i) β-aldolization of acetaldehyde [16,23] resulted in the formation of crotonaldehyde(II); (ii) acetaldehyde can be oxidized with the participation of surface oxygen [24] resulting in surface acetate(III); (iii) reduction of acetaldehyde through proton abstraction from surface OH groups [16] led to the formation of adsorbed ethoxy species (IV). Bands due to CO adsorbed on metallic sites with very low intensities were registered between 2200 and 1800 cm^{-1} (Fig. 1), which may be the consequences of the decomposition of acetaldehyde into CO and (possibly) methane.

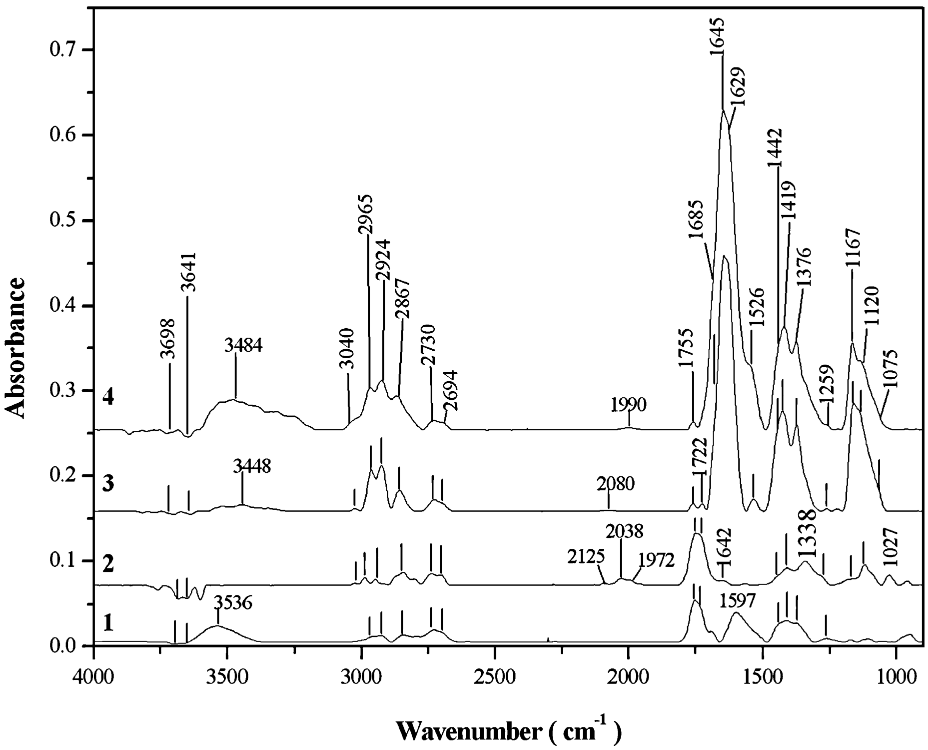

Fig. 1. IR spectra taken at 300 K after 60 min of acetaldehyde (1.33 hPa) adsorption on reduced catalysts: (1) TiO_2; (2) 1% Rh/TiO_2; (3) 1% Au/TiO_2; (4) 1% Pt/TiO_2.

Next the adsorbed layer produced on the surfaces of the catalysts by the adsorption of 1.33 hPa acetaldehyde at 300 K for 15 min and by a short (15 min) evacuation at 300 K was heated up quickly (30 s) to different temperatures then the samples were kept at each temperature for 1 min and they were cooled down to 300 K. IR spectra taken at 300 K after some treatments were collected for TiO_2 on and for 1% Pt/TiO_2 in Fig. 2.

The first obvious difference between the two sets of the spectra is that the bands are much more intense on Pt/TiO_2, than on TiO_2. This would suggest that the number of surface sites capable of coordinating acetaldehyde (and derived molecules) increases with the introduction of metal particles onto TiO_2. Other differences can be seen in the spectral range of 1800–900 cm^{-1}: while the band due to ν (C=C) (1598 cm^{-1}) of crotonaldehyde is dominant on TiO_2, the most intense bands of adsorbed crotonaldehyde are those due to ν (C=O) (1645 and 1629 cm^{-1}) on Pt/TiO_2. The band due to δ (C–H), on the other hand, is missing on Pt containing TiO_2. All these information led us to suppose that the coordination modes of crotonaldehyde are different on TiO_2 and on Pt/TiO_2. Very probably crotonaldehyde adsorbs on Lewis sites through one of the oxygen lone pairs on TiO_2 (similarly to one of the coordination modes of acetaldehyde), while crotonaldehyde may adsorb on the metallic sites via the C atom of its aldehyde group on Pt/TiO_2.

Another difference is the appearance of very small bands in the range of 2200–1800 cm^{-1} due to CO adsorbed on metallic sites. The formation of adsorbed CO is probably the consequence of the coordination mode of crotonaldehyde on Pt/TiO_2. The bands due to CO adsorbed on metallic sites were detected on Rh/TiO_2 and Au/TiO_2, too (Fig. 2).

With the increase of the temperature of the treatment the intensities of the bands monotonously decreased, but traces of the bands detected at lower temperatures can be observed even after the treatment at 673 K. The band due to ν (C=O) of acetaldehyde (1689 cm^{-1}) can be detected after the heat treatment at 673 K on TiO_2; this band, however, disappeared above 473 K from the spectra of Pt/TiO_2. The band due to ν_{as} (COO) of acetate at 1544 cm^{-1} appeared already at 300 K on the spectrum of Pt/TiO_2. This band at 1557 cm^{-1} was detected first after the heat treatment at 573 K on TiO_2. The broad absorptions attributed to H-bridge bonding disappeared at different temperatures depending on the nature of the catalysts: this absorption was completely missing at 373 K on Au/TiO_2, it disappeared at 423 K from the spectrum of TiO_2, on the spectra of Pt/TiO_2, however, it was observed with very low intensity even after the heat treatment at 573 K.

IR results obtained on Rh/TiO_2 were similar to those observed on TiO_2, while data registered on Au/TiO_2 were close to those on Pt/TiO_2.

During heating up and keeping of the samples at the desired temperature the desorbed products were monitored by mass spectrometer.

Acetaldehyde desorption from TiO_2, Au/TiO_2 and Pt/TiO_2 shows a maximum at 373 K, while maximum of acetaldehyde desorption was observed at 423 K from Rh/TiO_2. Above

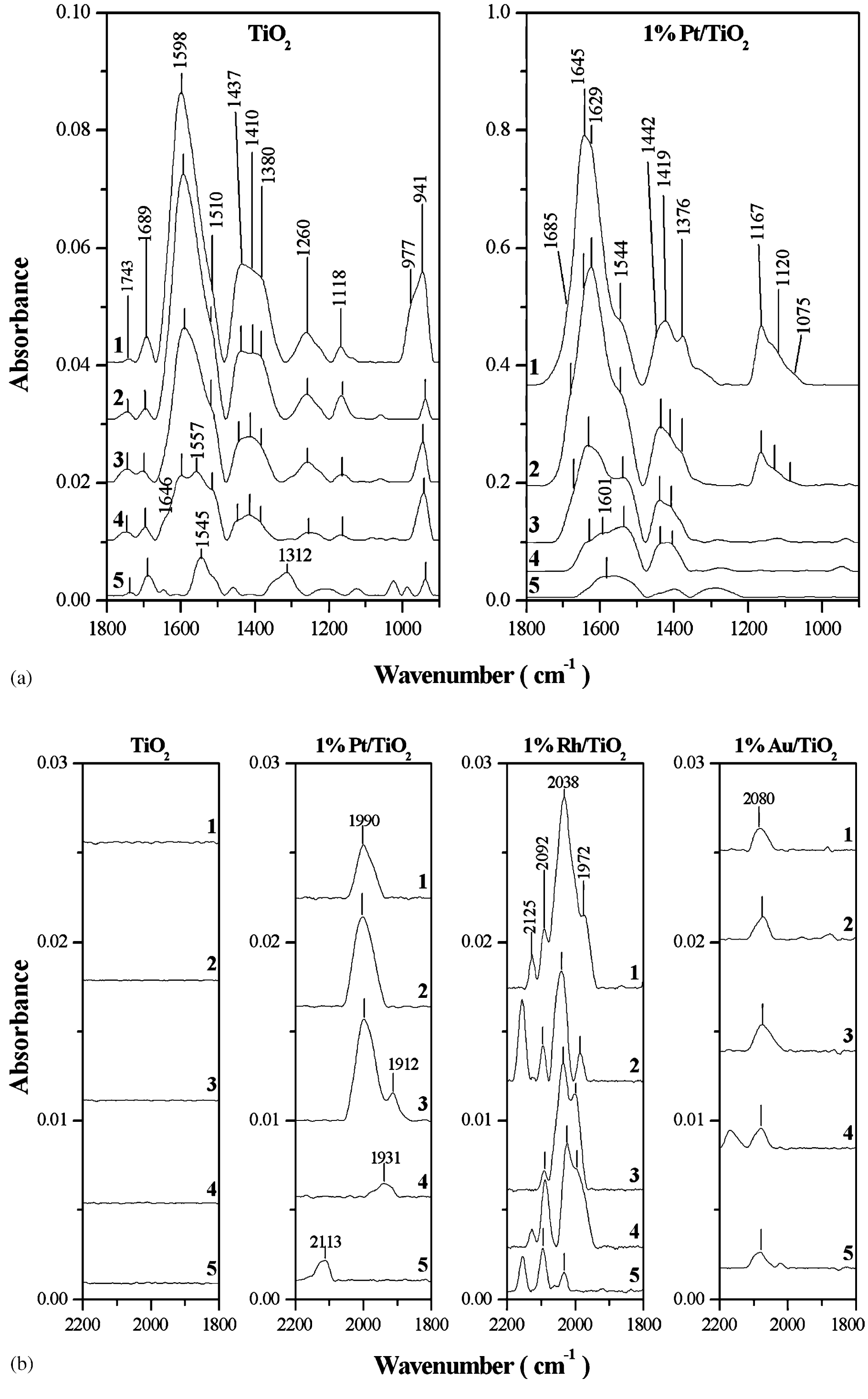

Fig. 2. IR spectra of adsorbed acetaldehyde layer on reduced catalysts after heat treatments (see text) at: (1) 300 K; (2) 373 K; (3) 473 K; (4) 573 K; (5) 673 K. The spectra were taken at 300 K.

523 K an increase in the amount of acetaldehyde desorbed from TiO_2-supported noble metals was registered. The two stages of acetaldehyde desorption from the catalysts can be connected with the two coordination modes of molecularly adsorbed acetaldehyde. The H-bridge bonded acetaldehyde proves to be the less stable surface form (T_{max} = 373–423 K). Acetaldehyde adsorbed on Lewis sites through one of the oxygen lone pairs (more stable species) can be the source of higher temperature acetaldehyde desorption.. The amount of desorbed acetaldehyde depended on the nature of the noble metals and it increases in the order of $TiO_2 < Rh/TiO_2 < Au/TiO_2 < Pt/TiO_2$ (Fig. 3).

Very small amount of water formed between 300 and 673 K on TiO_2 and on Rh/TiO_2. Water desorbs in two stages

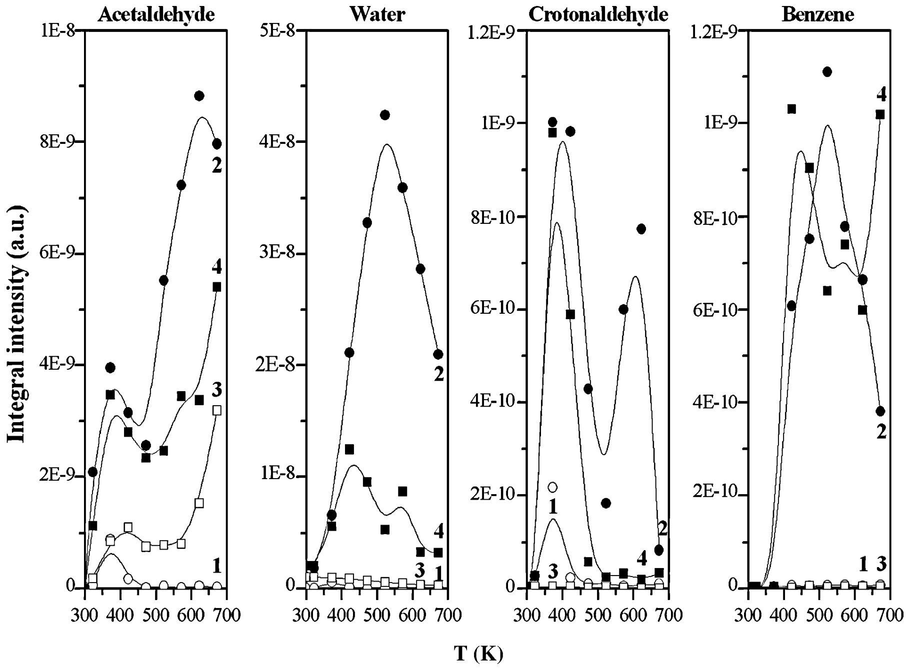

Fig. 3. Formation of some gas phase products (monitored by MS) during the heat treatments of adsorbed layer (see text) on reduced catalysts: (1) TiO_2; (2) 1% Pt/TiO_2; (3) 1% Rh/TiO_2; (4) 1% Au/TiO_2.

from Au/TiO_2 (at 423 K and at 573 K), while the greatest amount of water was measured from Pt/TiO_2 with at 523 K.

The amount of desorbed crotonaldehyde shows a maximum at 373 K on TiO_2, Au/TiO_2 and Pt/TiO_2. Desorption curve of crotonaldehyde depicts a high temperature peak at 623 K on Pt/TiO_2. No crotonaldehyde formation was observed on Rh/TiO_2.

T_{max} values for water do not match those for crotonaldehyde in the above experiments. Thus, it could not be possible to postulate a direct connection between water and crotonaldehyde productions on TiO_2-supported noble metals, i.e. there are no direct evidences for the occurrence of β-aldolization of acetaldehyde on these catalysts. This correlation was clearly demonstrated on oxides [25].

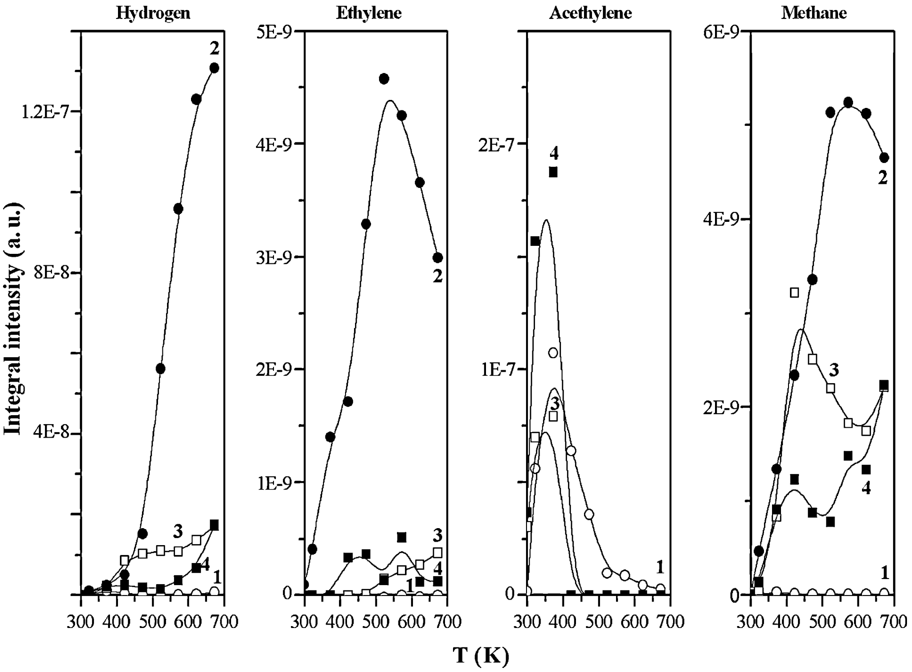

Fig. 4. Formation of some gas phase products (monitored by MS) during the heat treatments of adsorbed layer (see text) on reduced catalysts: (1) TiO_2; (2) 1% Pt/TiO_2; (3) 1% Rh/TiO_2; (4) 1% Au/TiO_2.

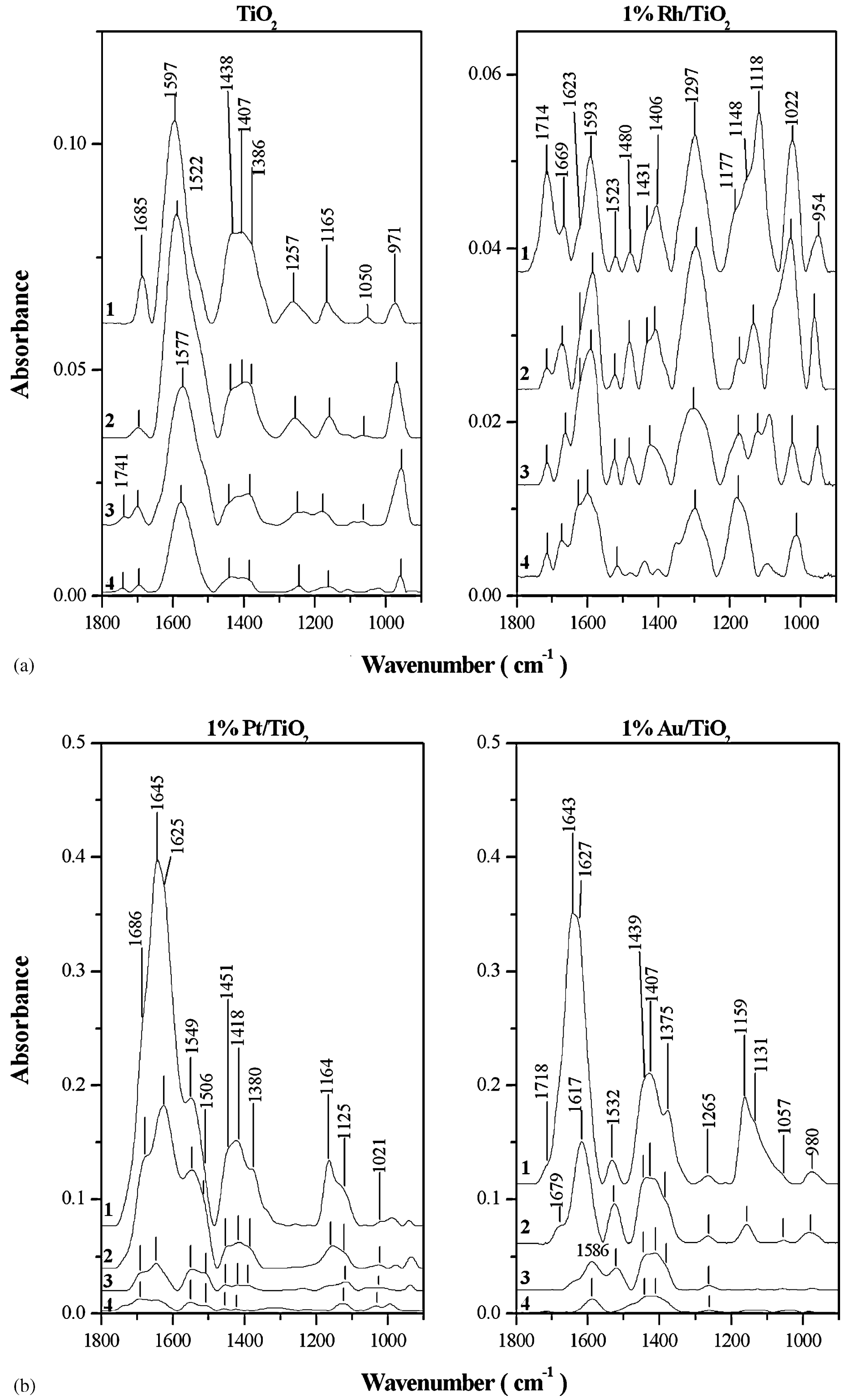

Fig. 5. Infrared spectra registered in isotherm experiments after 60 min on reduced catalysts: (a) TiO_2 and 1% Rh/TiO_2 (b) 1% Pt/TiO_2 and 1% Au/TiO_2; (1) 300 K; (2) 373 K; (3) 473 K; (4) 573 K. IR spectra were taken at the adsorption temperatures, the pressure of acetaldehyde was 1.33 hPa.

Negligible amount of benzene was produced on TiO_2 and Rh/TiO_2. Benzene formation from Au/TiO_2 and Pt/TiO_2 shows maximum at higher temperature than the T_{max} values for crotonaldehyde desorption (Fig. 3), indicating that benzene may form from crotonaldehyde.

Benzene production was interpreted by the reaction of crotonaldehyde with acetaldehyde (in the adsorbed layer) producing 2,4-hexadienal and water; 2,4-hexadienal suffers a C–H bond dissociation of the methyl group on metallic sites, which after intramolecular cyclization followed by

H_2O elimination may give benzene [26]. Although it turned out that no metallic sites are necessary for benzene production from the reaction of acetaldehyde with oxides [25], the catalytic effect of metallic sites on benzene formation can be clearly seen in Fig. 3. It is interesting to note that T_{max} values for H_2O and benzene formations are very similar on Pt/TiO_2 and on Au/TiO_2 (Fig. 3). According to the mechanism proposed in [26] both the formations of 2,4-hexadienal and benzene produce water, this would result in the same T_{max} values for water and benzene on the latter catalysts.

Above 423 K H_2 appeared among the desorption products on noble metal containing catalysts; practically no H_2 formation was detected on reduced TiO_2 (Fig. 4). The first appearance and the amount of H_2 depended on the nature of noble metals: the most effective catalyst was Pt/TiO_2, on which H_2 formation started at 423 K and the amount of H_2 was the highest. On Rh/TiO_2 the increase in the amount of gas phase H_2 began at 423 K, while H_2 production on Au/TiO_2 catalyst was observed only above 573 K. Ethylene was measured in the highest amount on Pt/TiO_2, and – in harmony with the data obtained on oxides [25] – no ethylene formation was detected on TiO_2 (Fig. 4).

Taking into account the relatively high temperatures of H_2 and C_2H_4 appearance in the gas phase, it can be stated that the more strongly bonded acetaldehyde would be the surface source of these products.

Interestingly, acetylene (considered as dehydrogenation product) was observed with $T_{max} = \sim 400$ K on TiO_2, Rh/TiO_2 and Au/TiO_2. No acetylene formation was detected on Pt/TiO_2. T_{max} of acetylene production would suggest a link between the desorption of H-bridge bonded acetaldehyde and the formation of acetylene. We have no clear explanation of this possible connection, yet.

CH_4, as the product of the acetate decomposition [16], appeared in the gas phase in the cases of noble metal containing TiO_2 catalysts above 400 K. No CH_4 formation was observed on TiO_2. The amount of CH_4 formed decreased in the order of Pt/TiO_2 > Rh/TiO_2 > Au/TiO_2.

Ethanol was produced only in heating up of the adsorbed acetaldehyde layer on TiO_2 (T_{max} = 373 K); on noble metal containing catalysts, however, ethanol formation was not observed. No CO and CO_2 appeared in the gas phase, neither from TiO_2, nor from noble metal/TiO_2 catalysts in these experiments.

The adsorption of acetaldehyde (1.33 hPa) has been further studied isothermally at 300–573 K on all catalysts. Spectra taken at the adsorption temperatures after 60 min have been collected in Fig. 5. Bands due to surface species (I)–(IV) appeared on all spectra registered at 300 K. From the comparison of the spectral range between 1800 and 1500 cm^{-1} detected at 300 K on TiO_2 and that of Pt/TiO_2 and Au/TiO_2 catalysts, it can be stated that crotonaldehyde coordination is different on TiO_2 and on the surfaces of noble metal containing TiO_2. The most intense band on TiO_2 spectrum appeared at 1597 cm^{-1} (ν (C=C) of adsorbed crotonaldehyde) in this range, while the bands at 1645–1643 and 1625–1627 cm^{-1} (ν (C=O) of adsorbed crotonaldehyde) were dominant on the spectra of Pt/TiO_2 and Au/TiO_2. It was supposed above that crotonaldehyde may adsorb on Lewis sites through one of the oxygen lone pairs on TiO_2, while crotonaldehyde is primarily adsorbed on the metallic sites via the C atom of its aldehyde group on Pt and Au containing TiO_2. On the spectrum of Rh/TiO_2 taken at 300 K both types of bands could be found. With the increase of the adsorption temperature, the intensities of the bands observed at 300 K monotonously decreased.

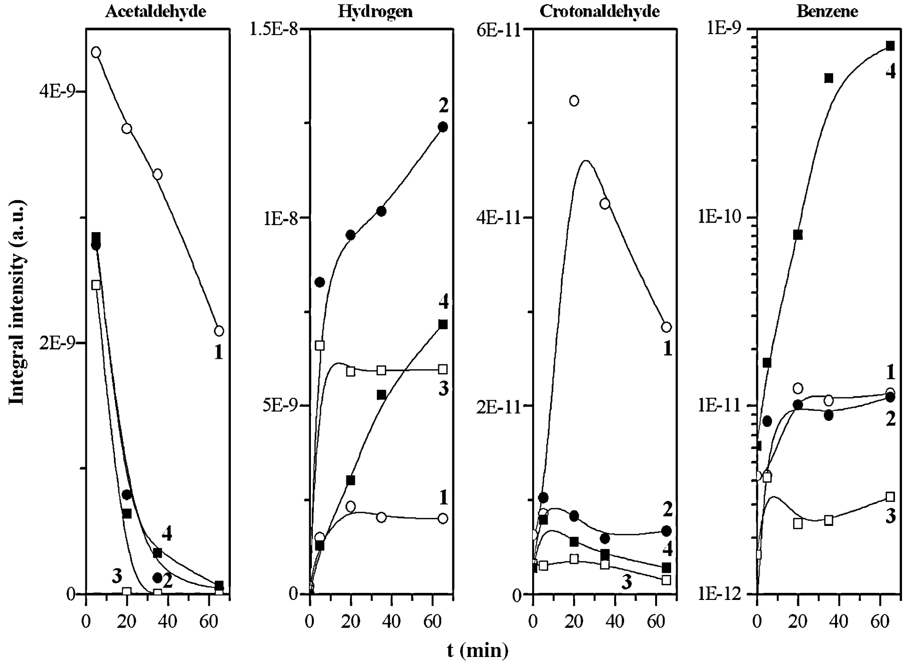

Fig. 6. Formation of some gaseous products (monitored by MS) at 573 K on reduced catalysts: (1) TiO_2; (2) 1% Pt/TiO_2; (3) 1% Rh/TiO_2; (4) 1% Au/TiO_2.

No new band(s) appeared indicating the formation(s) of new surface species.

At 300 and 373 K there were no appreciable changes in the gas phase composition during isothermal experiments. The consumption of acetaldehyde and the formation of different gas phase products were observed at 473–573 K indicating the occurrence of the acetaldehyde catalytic reactions with measurable rate above 373 K on these catalysts.

The rate and the extent of acetaldehyde consumption and that of the products' formation depended on the nature of the catalysts. Some data obtained at 573 K are collected in Fig. 6 for comparison.

The most effective catalyst in consuming of acetaldehyde proved to be Rh/TiO_2, while the less active was TiO_2. The presence of metal enhanced the formation of hydrogen: H_2 formed in the greatest amount on Pt/TiO_2. Crotonaldehyde was produced in the highest extent on TiO_2, on metal containing TiO_2 catalysts, however, only trace amount of crotonaldehyde was detected at 573 K. Au/TiO_2 showed the highest activity in benzene formation, while on Rh/TiO_2 practically no benzene production was observed. Commensurable little amount of benzene was produced on TiO_2 and Pt/TiO_2.

Formation of ethanol, CO and CO_2 was not observed in isotherm experiments.

4. Conclusions

1. Acetaldehyde adsorbs molecularly in two forms on the surfaces investigated: (i) producing H-bridge bonding on the OH groups and (ii) bonding through one of the oxygen lone pairs on Lewis sites.
2. Crotonaldehyde produced by β-aldolization of adsorbed acetaldehyde bonds either on Lewis sites of TiO_2 with one of its oxygen lone pairs, or on the metallic sites via the C atom of the aldehyde group.
3. H-bridge bonded acetaldehyde desorbs molecularly, while molecular acetaldehyde more strongly bonded on Lewis sites underwent mainly dehydrogenation.
4. The appearances and the amounts of gas phase products depended on the nature of the noble metals and on the reaction temperature.

Acknowledgement

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