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Adsorption and surface reactions of acetaldehyde on TiO_2 , CeO_2 and Al_2O_3

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Abstract

The adsorption and surface reactions of acetaldehyde at 300–673 K on TiO_2 , CeO_2 and Al_2O_3 were investigated by Fourier transform infrared spectroscopy and mass spectroscopy. Acetaldehyde adsorbs molecularly in two forms on the surfaces: (i) in a less stable H-bridge bonded form and (ii) in a more stable form adsorbed on Lewis sites through one of the oxygen lone pairs. Both forms of molecularly adsorbed acetaldehyde transform into crotonaldehyde ($\text{CH}_3\text{CH}=\text{CHCHO}$) by β -aldolization on the surfaces. The reaction of adsorbed acetaldehyde and crotonaldehyde resulted in the formation of benzene at higher temperature. The formation of crotonaldehyde and benzene depended on the nature and the pre-treatments of the oxides: the amount of crotonaldehyde was higher on H_2 -pre-treated, while the amount of benzene was higher on O_2 -pre-treated surfaces. Primarily the more strongly held acetaldehyde underwent dehydrogenation resulting in H_2 and acetylene. The formation of ethane was interpreted by hydrogenation of the transitorily formed ethylene and/or by catalytic decomposition of ethanol, which formed from adsorbed ethoxy produced by the surface reduction of acetaldehyde. Acetaldehyde could be oxidized into acetate, the decomposition of which resulted in gas phase methane. No CO and CO_2 was detected up to 673 K.

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Keywords: Acetaldehyde adsorption on oxides; FT-IR and MS; Surface species and gas-phase products; Crotonaldehyde and benzene formation

1. Introduction

The study of acetaldehyde transformations may be motivated by both applied and fundamental reasons. Acetaldehyde is one of the most abundant aldehydes in the atmosphere [1]. Environmental considerations need to study its non-catalytic reactions in the gas phase, in order to assess the consequences of its use as fuel or fuel additive [2–4]. Being aldehyde, acetaldehyde is also particularly undesirable in exhaust because of its potential carcinogen effects [5].

It has recently been found [6] 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. H_2 produced by steam

reforming of ethanol can be properly used in fuel cells or in electric vehicles ensuring the cleanest source of electric energy with practically zero emission of polluting gases. If, however, H_2 were produced catalytically from ethanol in the vehicles, the presence of acetaldehyde in the exhaust would represent high danger to the environment. Thus, its catalytic transformation (to less dangerous materials) would play a vital role.

Acetaldehyde on the other hand may be starting material for the catalytic production of acetone, diethyl ketone [7], ethanol, crotonaldehyde, butene and butadiene [8]. Data obtained in the study of the adsorption and further (surface) reactions of acetaldehyde would contribute to the deeper understanding of the reaction mechanisms of the above processes.

In the present work surface species formed during the adsorption of acetaldehyde on TiO_2 , CeO_2 and Al_2O_3 were studied by FT-IR and the gas-phase products produced during the interaction between acetaldehyde and the oxides

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were analyzed by mass spectrometry. The oxides studied in this study differ in their reducibility and they are frequently used as catalyst support.

2. Experimental

The following oxides were used: TiO₂ (Degussa P25, 50 m²/g), CeO₂ (Ventron 4 m²/g), and Al₂O₃ (Degussa P110 C1, 100 m²/g).

For IR studies the oxides were pressed onto a Ta-mesh (30 mm × 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 pre-treatments of the samples were performed in a stainless steel UV IR cell (base pressure 1.33×10^{-5} Pa): (a) the sample was heated in 1.33 hPa of O₂ up to 573 K and it was kept at this temperature for 1 h (O₂-pre-treated surface); or (b) it was heated in 1.33 hPa of H₂ up to 573 K and it was kept at this temperature for 1 h (H₂-pre-treated surface). 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.

Acetaldehyde was the product of Riedel de Haen (99.8%); before its admission to the oxides it was purified by freeze and pump method.

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 CO₂- and H₂O-free air generated by a Balston 75–62 FT-IR purge gas generator. The spectrum of the pre-treated 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, which was connected with the UV IR cell via a leak valve. Differential evacuation ensured 6.65×10^{-4} Pa around the

MS head when reacting gases were present in the cell and the leak valve was opened. 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

On the spectra registered in 1.33 Pa acetaldehyde on oxygen pre-treated oxides at 300 K bands due to molecularly adsorbed acetaldehyde (ν_{as} (CH₃) at 2960–2968 cm⁻¹, ν_{s} (CH₃) at 2916–2924 cm⁻¹, ν (CH) at 2723–2732 cm⁻¹, ν (C=O) at 1686–1729 cm⁻¹, δ_{as} (CH₃) at 1407–1449 cm⁻¹, δ (CH) at 1366–1386 cm⁻¹, δ_{s} (CH₃) at 1334 cm⁻¹ and γ (CH₃), ν (C–C) at 1110–1139 cm⁻¹, Table 1) can be clearly identified. The intensities of these bands increased with the increase of acetaldehyde pressure up to 1.33 hPa. Spectra obtained on Al₂O₃ are depicted in Fig. 1. In 1.33 hPa of acetaldehyde the bands of the gas-phase acetaldehyde (2732, 2700, 1753 and 1723 cm⁻¹) became dominant. Similar spectral changes were observed on TiO₂ and CeO₂.

As concerns the modes of acetaldehyde coordination to the oxide surfaces, the relevant shift down of the acetaldehyde C=O stretching (from 1730 to 1686–1706 cm⁻¹) may suggest that a part of acetaldehyde is coordinated on Lewis acid sites through one of the oxygen lone pairs. Spectroscopic features observed above 3400 cm⁻¹ revealed another coordination mode of molecular acetaldehyde on the oxidic surfaces. The negative features (at 3711 and 3665 cm⁻¹ on TiO₂, at 3760, 3732 and

Table 1
Bands (in cm⁻¹) and their assignments observed in acetaldehyde adsorption on various metal oxides

Assignment	Gas [9]	Gas ^a	TiO ₂ [10] (anatase)	SiO ₂ [11]	β-UO ₃ [12]	UO ₂ [12]	TiO ₂ ^a	CeO ₂ ^a	Al ₂ O ₃ ^a
ν_{as} (CH ₃)	3003	2998 2964	2969	2988	2984	2987	2960	2968	2963
ν_{s} (CH ₃)	2918	2931	2914	2914	2907	2934	2923	2916	2924
ν (CH)	–	2730	–	–	–	–	2727	2723	2732
ν (C=O)	1722	1750 1730	1718	1724	1706	1705	1729–1686	1717–1706	1723–1694
δ_{as} (CH ₃)	1422	1454	–	1448	1412	1450	1440–1434	1409–1407	1449–1448
δ (CH)	1389	1412	–	1388	1380	1380	1386–1372	1378–1366	1380–1374
δ_{s} (CH ₃)	1352	1365 1335	1355	1356	1351	1340	1334	–	–
γ (CH ₃), ν (C–C)	1120	1118	–	–	1125	1123	1139–1110	1121–1114	1118–1116

^a This work.

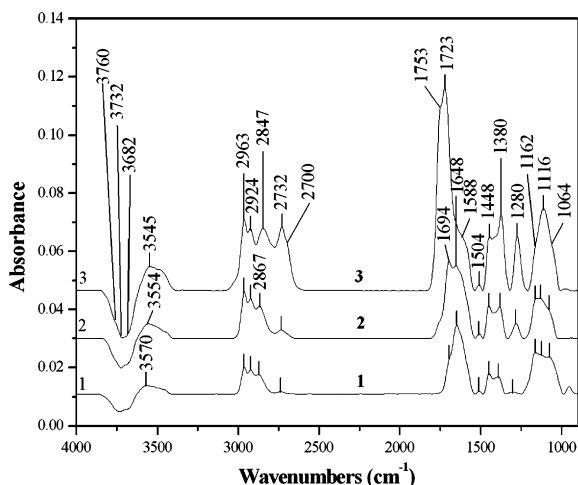


Fig. 1. The effect of acetaldehyde vapor pressure at 300 K on the IR spectra of O_2 -pre-treated Al_2O_3 : (1) 1.33 Pa; (2) 13.3 Pa; (3) 1.33 hPa. Adsorption time 15 min.

3682 cm^{-1} on Al_2O_3) and broad absorptions (centered at 3440 cm^{-1} on TiO_2 and at 3570 (in 1.33 Pa)– 3545 (in 1.33 hPa) cm^{-1} on Al_2O_3) show that another part of acetaldehyde may adsorb through H-bridge bonding on TiO_2 and Al_2O_3 surfaces. No spectroscopic evidences for H-bridge bonding were registered on the spectra of CeO_2 .

Besides the bands of molecularly adsorbed acetaldehyde (I) several absorptions appeared on the spectra showing the immediate surface transformations of acetaldehyde both on O_2 - and H_2 -pre-treated oxides already at 300 K.

Among these absorptions the bands at 1663 – 1638 cm^{-1} ($\nu(\text{C}=\text{O})$), at 1596 – 1586 cm^{-1} ($\nu(\text{C}=\text{C})$), at 1260 – 1280 cm^{-1} ($\delta(\text{C}-\text{H})$), at 1173 – 1160 cm^{-1} ($\nu(\text{CC})$, $\rho(\text{CH}_3)$) and at 936 – 981 cm^{-1} ($\rho(\text{CH}_3)$) can be attributed to adsorbed crotonaldehyde (II) ($\text{CH}_3\text{CH}=\text{CHCHO}$) [8,13–15], which is produced by β -aldolization occurring between two acetaldehyde molecules on the surface [8,12].

The bands at 2868 – 2843 cm^{-1} ($\nu_s(\text{CH})$) and at 1079 – 1037 cm^{-1} ($\nu(\text{C}=\text{O})$) may be assigned to adsorbed ethoxy (IV) ($\text{CH}_3\text{CH}_2\text{O}_{(\text{a})}$) species [8], which might be the product of reduction of acetaldehyde on the oxide surfaces through proton abstraction from surface OH groups.

The band at 1546 – 1542 cm^{-1} ($\nu_{\text{as}}(\text{COO})$) appeared on oxidized TiO_2 and CeO_2 may be due to surface acetate (III) ($\text{CH}_3\text{COO}_{(\text{a})}$) [8,13,14,16], which is the result of acetaldehyde oxidation on surface oxygen (S–O) sites [17].

The reduction of the oxides led to the overall diminution of the bands, the bands due to molecularly adsorbed acetaldehyde (see above), however, can be clearly distinguished.

In the next experiments the adsorbed layer of acetaldehyde on different oxides was produced by the adsorption of 1.33 hPa acetaldehyde at 300 K for 15 min. After a short (15 min) evacuation at 300 K the samples were heated up quickly (30 s) to different temperatures, they were kept at each temperature for 1 min, and then they were cooled down

to 300 K. The IR spectra taken at 300 K after some heat treatments were collected in Fig. 2 for oxides preliminary pre-treated with oxygen.

Bands on the spectra due to adsorbed layer produced at 300 K show the presence of molecularly adsorbed acetaldehyde (I), crotonaldehyde (II), acetate (III) and ethoxy (IV) species.

The elimination of the band at 1700 – 1685 cm^{-1} (assigned to $\nu(\text{CO})$ of adsorbed acetaldehyde) up to about 423 K was accompanied by the continuous disappearance of the broad absorptions due to H-bridge bonding (at 3440 – 3536 cm^{-1} on TiO_2 and at 3545 – 3570 cm^{-1} on Al_2O_3 —not shown). From this we propose that the bands at 1700 – 1685 cm^{-1} are partly due to $\nu(\text{CO})$ of acetaldehyde adsorbed by H-bridge bonding through the surface OH groups of the oxides.

The surface concentrations of (I)–(IV) surface species drastically decreased with the increase of the temperature above 473 K; their traces, however, could be detected even after a treatment at 673 K. On Al_2O_3 the band due to surface acetate (1551 cm^{-1}) was observed only after the heat treatment at 673 K.

During heating up and keeping of the samples at the desired temperature the desorbed products were monitored by mass spectrometer (Fig. 3). Acetaldehyde desorption shows small maximum at 423 K on all O_2 -pre-treated surfaces; this feature corresponds well to the elimination of H-bridge-bonded acetaldehyde presented by the IR results. The amounts of acetaldehyde desorbed above 423 K, however, permit the conclusion that a part of acetaldehyde bonds more strongly at the Lewis sites of these oxides. Water formed with $T_{\text{max}} = 423\text{ K}$ and $T_{\text{max}} = 473\text{ K}$ on O_2 -pre-treated CeO_2 and TiO_2 , respectively. No water formation was detected on O_2 -pre-treated Al_2O_3 . The production of crotonaldehyde on O_2 -pre-treated CeO_2 and TiO_2 shows the same T_{max} as that of water. Benzene formation depicts maxima at 573 K on CeO_2 and TiO_2 ; no benzene was found on Al_2O_3 .

The H_2 -pre-treatment of the oxides led to the overall diminution of the IR bands. Interestingly, the stability of adsorbed acetaldehyde and crotonaldehyde was higher on reduced surfaces, as the bands due to these surface species disappeared at higher temperature on reduced oxides.

Acetaldehyde desorption from H_2 -pre-treated TiO_2 shows a maximum at 373 K, while acetaldehyde desorbs in two stages ($T_{\text{max}} = \sim 400$ and 623 K) from H_2 -pre-treated Al_2O_3 . The amount of acetaldehyde desorbed from H_2 -pre-treated CeO_2 increased up to 423 K, it was practically constant between 423 and 623 K, and above this temperature increased again (Fig. 4).

The temperature range observed in the IR studies (300–423 K) for the disappearance of acetaldehyde H-bridge bonded corresponds well to the first stage of acetaldehyde desorption monitored by mass spectrometer. From these data it seems to be obvious that molecular acetaldehyde bonding by H-bridge to the surface is a less stable molecular form of

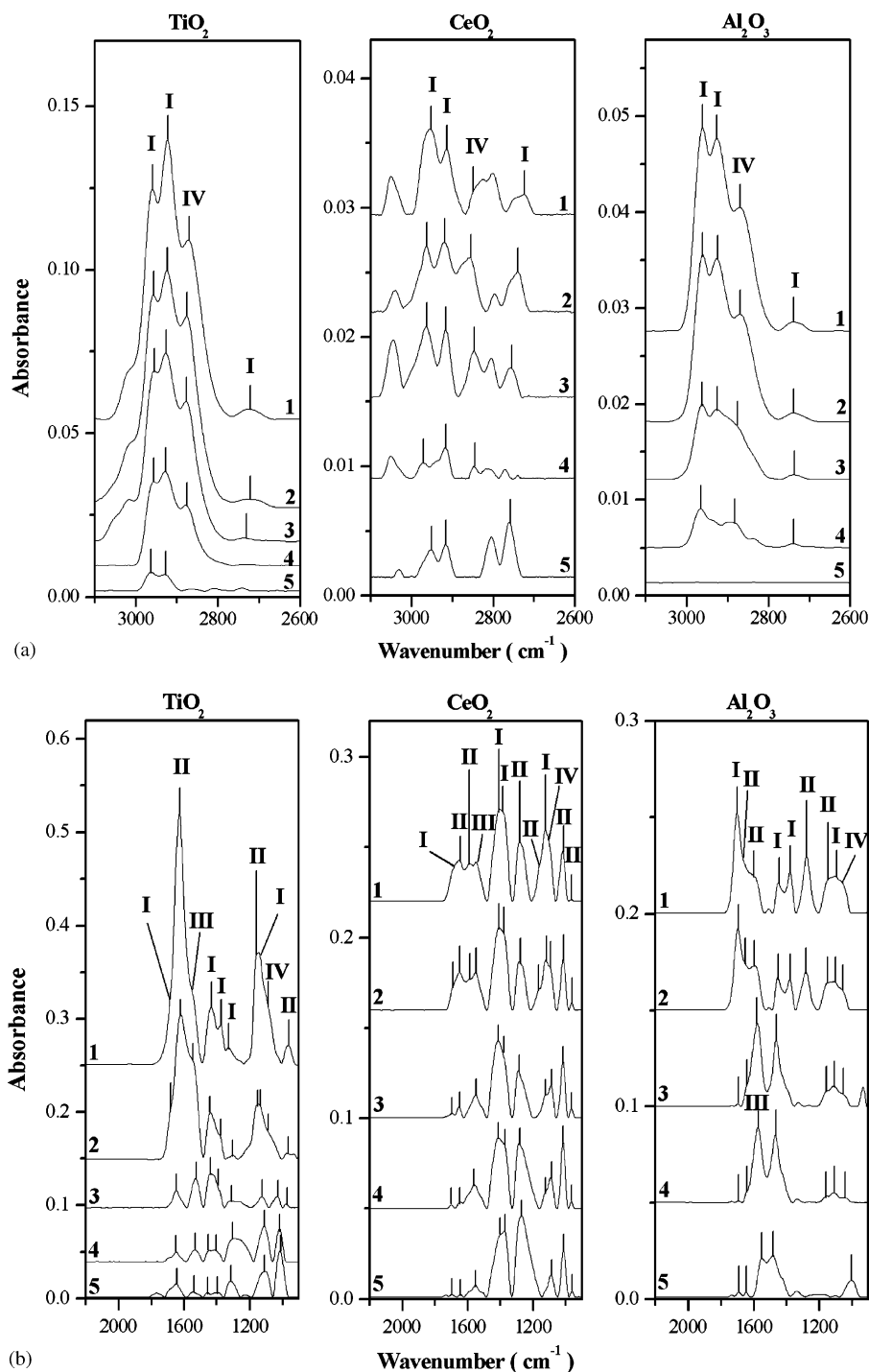


Fig. 2. IR spectra of adsorbed acetaldehyde layer on O_2 -pre-treated oxides after heat treatments (see text) at: (1) 300 K; (2) 373 K; (3) 473 K; (4) 573 K; (5) 673 K. The spectra were taken at 300 K.

adsorbed acetaldehyde, which leaves the surface in molecular form up to 423 K.

The evolution of water from the adsorbed layer produced on reduced TiO_2 and Al_2O_3 shows great similarities to that of molecular acetaldehyde (Fig. 4). Practically no water formation was experienced on CeO_2 . T_{max} values of

crotonaldehyde desorption are the same as T_{max} values of molecular acetaldehyde desorption from H-bridge bonded forms on these surfaces. All these information permit the conclusion that a part of the hydrogen-bridge bonded acetaldehyde underwent β -aldol condensation producing water and crotonaldehyde up to 423 K on TiO_2 and on

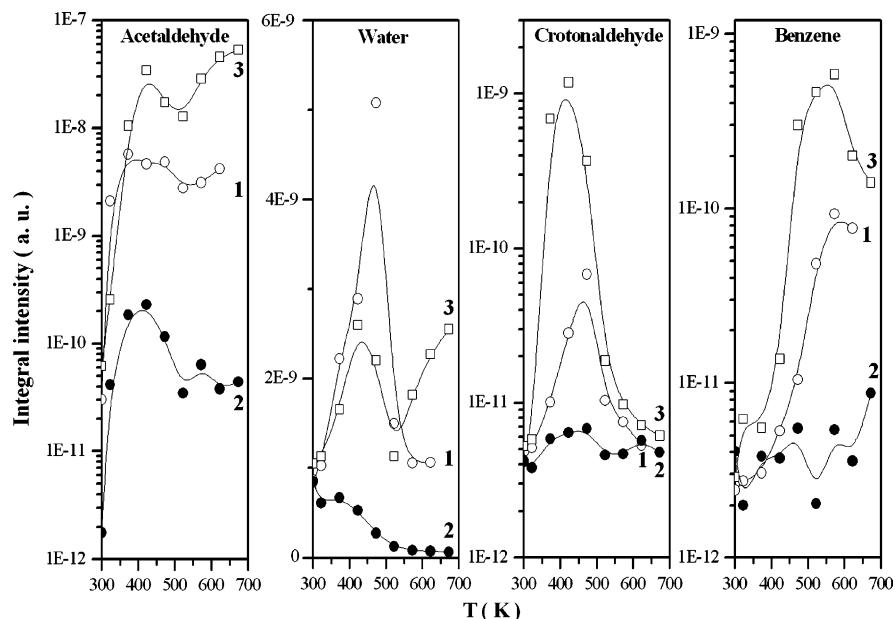
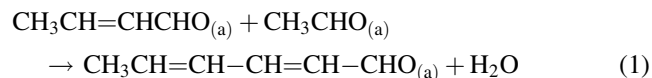


Fig. 3. Formation of some gas-phase products (monitored by MS) during the heat treatments of adsorbed layer (see text) on O_2 -pre-treated oxides: (1) TiO_2 ; (2) Al_2O_3 ; (3) CeO_2 .

Al_2O_3 . On CeO_2 , where no signs for H-bridge bonded acetaldehyde were detected by IR, crotonaldehyde formation shows a maximum at higher temperature.

The first T_{max} of benzene formation appeared at somewhat higher temperature (423 K), than that of crotonaldehyde production on TiO_2 (373 K) and Al_2O_3 (~400 K). Formerly [18] the benzene formation in the interaction of ethanol with Pt/CeO_2 was interpreted by the reaction of crotonaldehyde (formed in β -aldolization of acetaldehyde) with acetaldehyde (produced

in the dehydrogenation of ethanol) producing 2,4-hexadienal:



It has been further proposed that 2,4-hexadienal suffers a C–H bond dissociation of the methyl group on Pt, which after intramolecular cyclization followed by H_2O elimination may give benzene.

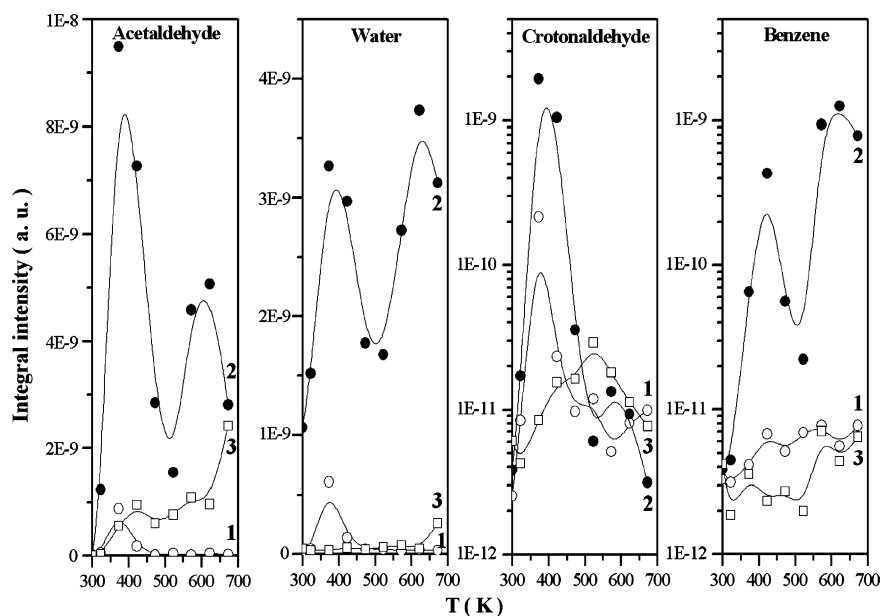


Fig. 4. Formation of some gas-phase products (monitored by MS) during the heat treatments of adsorbed layer (see text) on H_2 -pre-treated oxides: (1) TiO_2 ; (2) Al_2O_3 ; (3) CeO_2 .

Our data suggest that no metallic sites are necessary for the benzene formation in the interaction of acetaldehyde with the surfaces of oxides. Similar conclusion can be drawn from the data obtained on UO_2 (1 1 1) single crystal [19] and on TiO_2 [20].

Another part of molecular acetaldehyde adsorbing on Lewis acid sites through one of the oxygen lone pairs proved to be more stable on CeO_2 and Al_2O_3 , as desorption of molecular acetaldehyde was also detected above 423 K from these surfaces. Acetaldehyde desorption shows a high

temperature maximum at 623 K from H_2 -pre-treated Al_2O_3 and the amount of acetaldehyde desorbed from H_2 -pre-treated CeO_2 increased above 623 K (Fig. 4). Above 473 K no acetaldehyde desorption was detected from reduced TiO_2 .

On H_2 -pre-treated CeO_2 , where no signs for H-bridge bonded acetaldehyde were detected by IR, crotonaldehyde formation shows a maximum at 523 K, and small maxima at 523 and 573 K can be distinguished in crotonaldehyde formation from H_2 -pre-treated TiO_2 and Al_2O_3 .

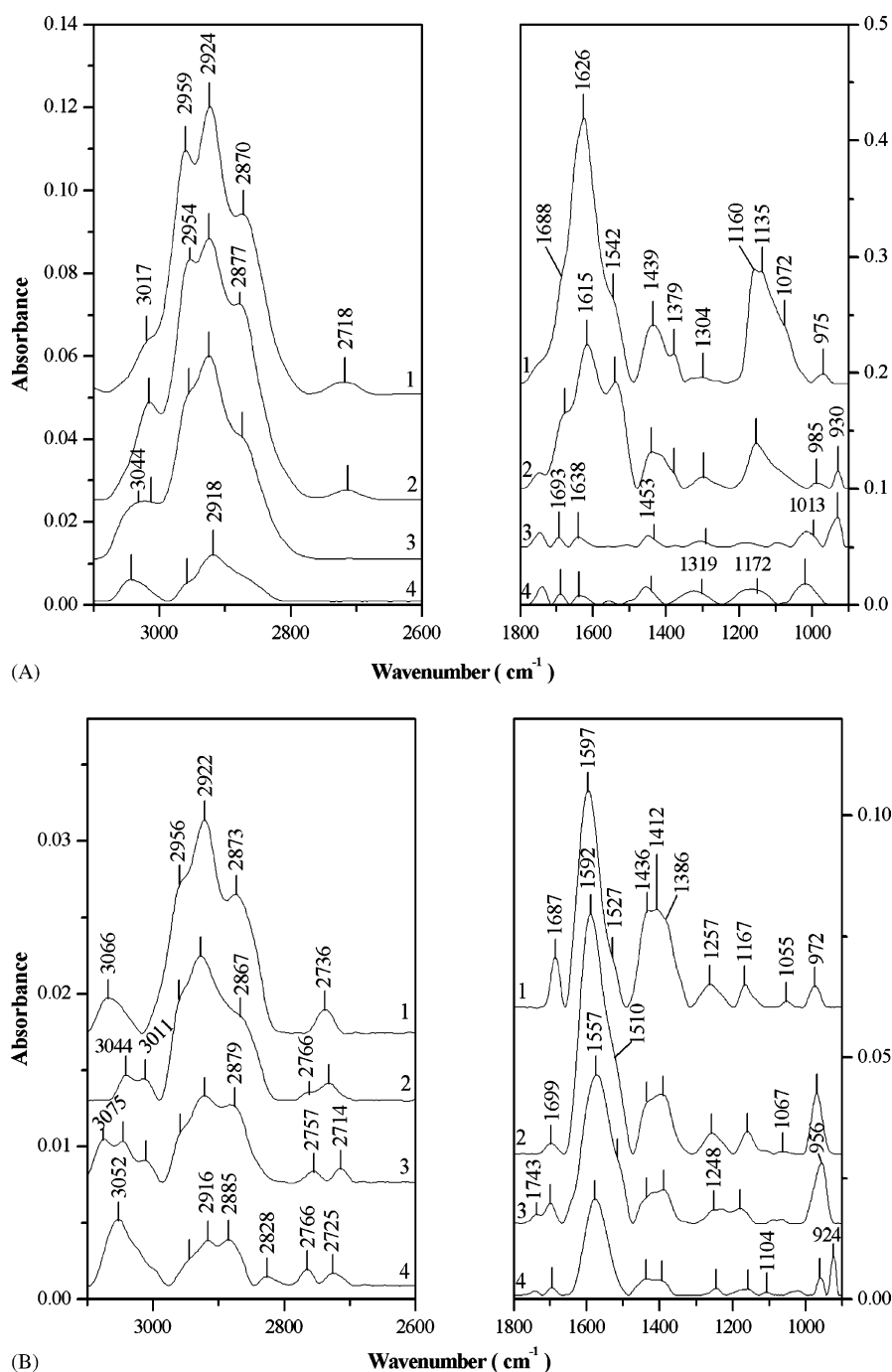


Fig. 5. Infrared spectra registered in isotherm experiments after 60 min on O_2 -pre-treated TiO_2 (A) and on H_2 -pre-treated TiO_2 (B): (1) 300 K; (2) 373 K; (3) 473 K; (4) 573 K. IR spectra were taken at the adsorption temperatures; the pressure of acetaldehyde was 1.33 hPa.

Following the formation of crotonaldehyde above 423 K, a maximum at 623 K on H_2 -pre-treated Al_2O_3 and a small maximum at 573 K on H_2 -pre-treated TiO_2 were observed in the curves due to benzene formation. Above $T_{\text{max}} = 523$ K of crotonaldehyde production, the amount of benzene slightly increased on H_2 -pre-treated CeO_2 (Fig. 4).

Besides its surface transformation into crotonaldehyde and benzene, adsorbed acetaldehyde underwent dehydrogenation during the above heat treatments both on O_2 -pre-treated and H_2 -pre-treated oxides. This is manifested in the

detection of hydrogen and acetylene on all H_2 -pre-treated surfaces and on O_2 -pre-treated CeO_2 . The more awaited dehydrogenation product, ethylene, formed only on Al_2O_3 (both on O_2 - and H_2 -pre-treated) and traces of ethylene were detected on H_2 -pre-treated TiO_2 . Interestingly, ethane formation was detected on all surfaces. The lack of ethylene among the desorption products on TiO_2 and CeO_2 may suggest that the hydrogenation of ethylene might lead to the formation of ethane on these surfaces. The simultaneous detection of ethylene and ethane on

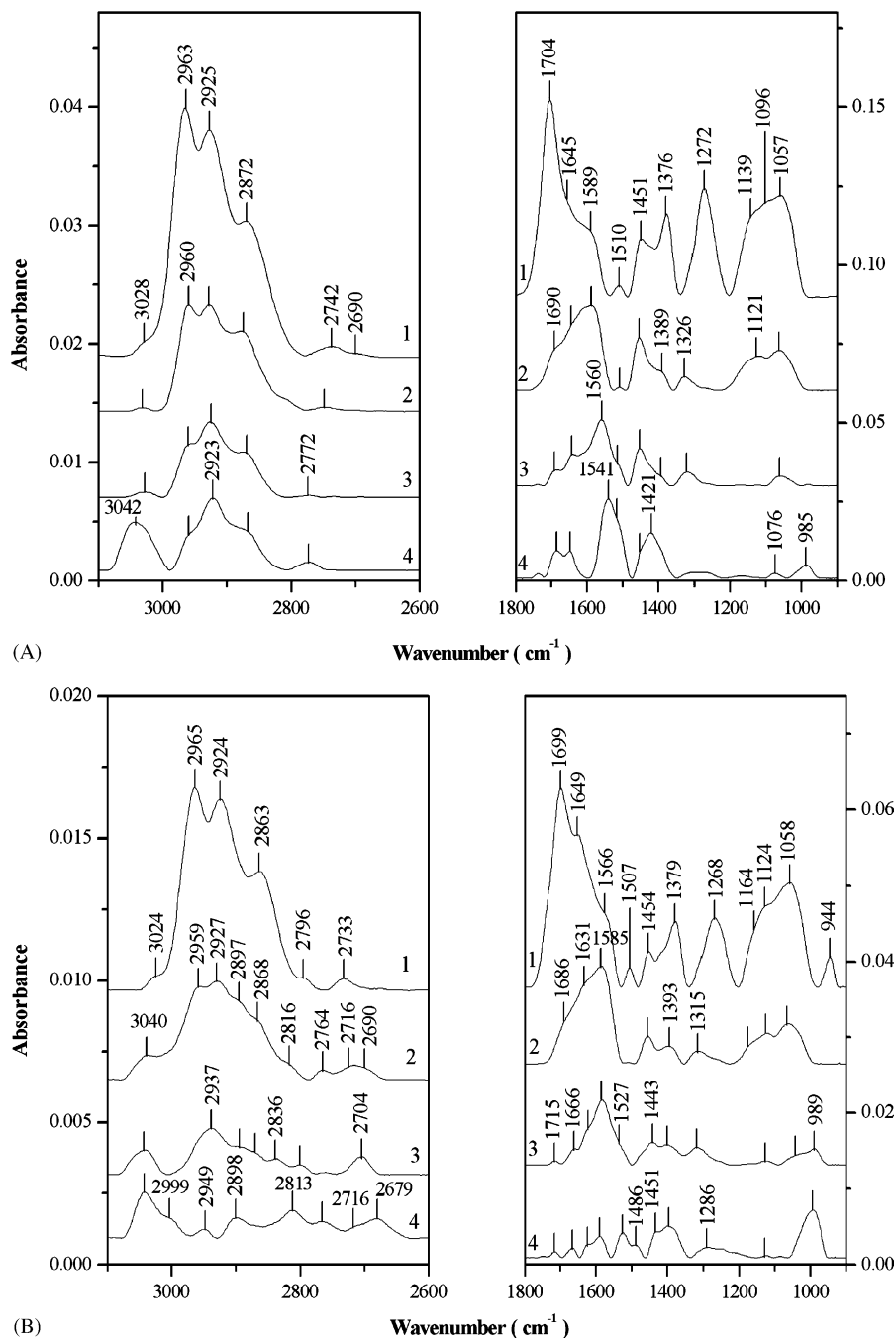


Fig. 6. Infrared spectra registered in isotherm experiments after 60 min on O_2 -pre-treated Al_2O_3 (A) and on H_2 -pre-treated Al_2O_3 (B): (1) 300 K; (2) 373 K; (3) 473 K; (4) 573 K. IR spectra were taken at the adsorption temperatures; the pressure of acetaldehyde was 1.33 hPa.

Al_2O_3 surfaces, however, contradicts to the above suggestion.

Ethoxy surface species formed in the reduction of acetaldehyde (Fig. 2) are the possible sources of the appearance of ethanol among the desorption products on all surfaces except H_2 -pre-treated Al_2O_3 . We note that the catalytic decomposition of ethanol could also lead to the formation of ethane [6]. The appearance of CH_4 in the gas phase is possibly the consequence of acetate decomposition [8].

It is to be noted that neither CO , nor CO_2 was detected up to 673 K.

Next the interaction of acetaldehyde with the oxides (both O_2 - and H_2 -pre-treated) was investigated isothermally at 300–573 K. IR spectra were registered at the reaction temperatures; the base spectrum and the actual gas-phase spectrum were subtracted from the spectra taken in the presence of acetaldehyde vapor. The spectra obtained in the above subtractions for TiO_2 and for Al_2O_3 are shown in Figs. 5 and 6, respectively. Bands due

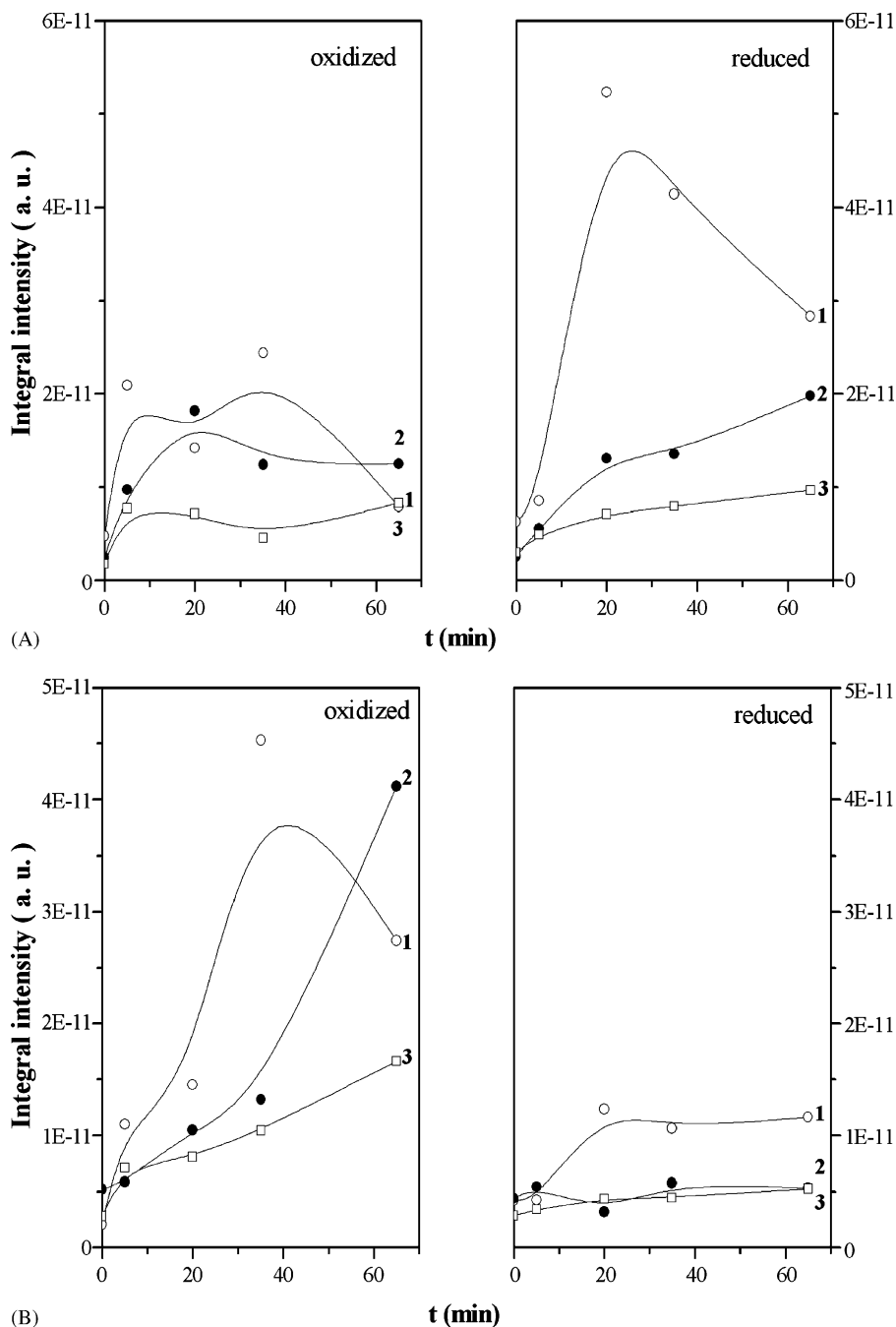


Fig. 7. Formation of crotonaldehyde (A) and benzene (B) at 573 K in isotherm experiments on O_2 -pre-treated and H_2 -pre-treated oxides: (1) TiO_2 ; (2) Al_2O_3 ; (3) CeO_2 .

to the surface species (I)–(IV) (see above) appeared on the spectra of TiO_2 already at 300 K. On Al_2O_3 the band due to acetate (1527 cm^{-1}) could be detected only at 573 K.

It can be generally stated that the pre-treatment with H_2 led to the overall diminution of the bands on both oxides. The IR spectra registered on TiO_2 (Fig. 5A and B), however, seem to be more affected by the reduction, than those obtained on Al_2O_3 (Fig. 6A and B). As concerns the effect of the pre-treatments, data obtained on O_2 - and H_2 -pre-treated CeO_2 were similar to that observed on Al_2O_3 .

Dramatic changes occurred at and above 473 K, where the intensities of the bands drastically decreased and/or some bands disappeared.

Parallel with the infrared measurements the changes in the gas phase composition were also monitored by mass spectrometer.

In harmony with the IR data there were no dramatic changes in the gas phase composition at 300–373 K. Above 373 K, however, the amount of hydrogen increased with the increase of the reaction temperature. The extent of this increase was higher on H_2 -pre-treated TiO_2 and CeO_2 in comparison with O_2 -pre-treated TiO_2 and CeO_2 . On Al_2O_3 pre-treated by O_2 a detectable increase in the amount of hydrogen was observed only at 573 K. On H_2 -pre-treated Al_2O_3 , however, the increase of the reaction temperature did not influence the hydrogen production.

The amount of methane (presumably the gas-phase product of surface acetate decomposition) decreased with the increase of the reaction temperature irrespective of the nature and the pre-treatments of the oxides.

Although the bands due to surface ethoxy were detected practically in the whole temperature range, a very small amount of ethanol was detected only at 300 K on TiO_2 (both O_2 - and H_2 -pre-treated). This is presumably due to the rapid catalytic transformation/decomposition of ethanol (if formed) on the other oxides and at other temperatures.

Special attention has been paid to the formations of crotonaldehyde and benzene. The amount of crotonaldehyde did not change with the increase of the reaction temperature between 300 and 473 K. At 573 K the increase of gas phase crotonaldehyde was observed on all samples; the amount of crotonaldehyde measured at 573 K depended on the nature and on the pre-treatments of the oxides (Fig. 7A and B). Somewhat higher amounts of crotonaldehyde were detected on H_2 -pre-treated oxides. Benzene formed in detectable amounts only at 573 K. Interestingly, the amounts of benzene were higher on O_2 - than on H_2 -pre-treated oxides (Fig. 7B). From these findings it can be concluded that in the interaction of acetaldehyde with oxides the crotonaldehyde formation would be enhanced by the presence of surface Lewis sites and OH groups (H_2 -pre-treated surfaces), while the

benzene production might be increased by the active surface oxygen sites (O_2 -pre-treated surfaces) of the oxides.

4. Conclusions

1. Acetaldehyde adsorbs molecularly on oxides through surface OH groups forming hydrogen bridge bonding (less stable form) and through one of oxygen lone pairs on Lewis surface sites (more stable form).
2. Adsorbed acetaldehyde transforms by β -aldolization into crotonaldehyde, by oxidation into acetate and by reduction into ethoxy on the oxides.
3. At higher temperatures benzene forms via the reaction of acetaldehyde and crotonaldehyde, and the more stable molecularly adsorbed acetaldehyde underwent dehydrogenation.
4. The pre-treatments of the oxides affected the surface concentrations and the gas phase appearance of the above products.

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