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Adsorption and surface reactions of acetaldehyde on alumina-supported noble metal catalysts

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Adsorption and further surface transformations of acetaldehyde on Al_2O_3-supported noble metal catalysts were studied by FTIR spectroscopy. Two forms (H-bridge bonded and bonded to Lewis sites) of molecularly adsorbed acetaldehyde were detected. β-aldolization of acetaldehyde into crotonaldehyde was observed already at 300 K on all surfaces investigated. The formation of adsorbed crotonaldehyde depended on the temperature and on the nature of the metal. The gas phase products (crotonaldehyde, benzene, hydrogen, ethane, ethylene and acetylene) were analyzed by mass spectrometer. Their appearance in the gas phase and their amounts depended on the nature of the metal and on the temperature.

KEY WORDS: acetaldehyde adsorption; Al_2O_3-supported Pt, Rh, Au catalysts; surface species; gas phase products; FTIR; MS.

1. Introduction

The demand for alternative sources of energy initiated the studies on steam reforming of ethanol producing H_2-rich (CO-free) gas mixture [1–13]. The use of H_2 as fuel ensures the cleanest source of energy with practically zero emission of polluting gases. If, however, H_2 is be produced catalytically, acetaldehyde appears both in the gas phase and in the adsorbed layer [14]. The presence of acetaldehyde in the exhaust would be dangerous to the environment because of its potential carcinogen effects [15]. From this point of view the catalytic transformation of acetaldehyde into less hazardous materials seems to be very important.

Al_2O_3-supported noble metal catalysts proved to be the most active in producing H_2 from ethanol + water gas mixture [13]. Accordingly, acetaldehyde (considered as the indicator of hydrogen production) may be formed most effectively on these catalysts. In the present work we publish data on the adsorption and further surface reactions of acetaldehyde on Al_2O_3-supported noble metals. Our primary aim was to assign the surface species and gas phase products of the interaction between acetaldehyde and these catalysts and to probe the effectivity of these catalysts in the catalytic transformation of acetaldehyde.

2. Experimental

Al_2O_3 was the product of Degussa (P110 C1, 100 m^2/g). About 1% Pt/Al_2O_3 and 1% Rh/Al_2O_3 catalysts were prepared by impregnating of Al_2O_3 with an aqueous solution of $H_2PtCl_6 \times 3H_2O$ (Reanal) and with that of $RhCl_3 \times 3\ H_2O$ (Johnson Matthey), respectively. The impregnated powders were dried at 383 K for 3 h. Al_2O_3 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 × 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 pre-treatments 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.

Infrared spectra were recorded with a Genesis (Mattson) FTIR spectrometer with a wavenumber accuracy of $\pm 4\ cm^{-1}$. 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 pre-treated sample

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(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 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 adsorption of 1.33 Pa acetaldehyde at 300 K on reduced catalysts resulted in the IR spectra collected on figure 1. The bands at 2963 cm^{-1} ($\nu_{as}(CH_3)$), at 2923 cm^{-1} ($\nu_s(CH_3)$), at 1692 cm^{-1} ($\nu(C=O)$), at 1451 cm^{-1} ($\delta_{as}(CH_3)$) and at 1391 cm^{-1} ($\delta(CH)$) belong to molecularly adsorbed acetaldehyde (I). The appearance of other bands is the consequence of surface transformation of acetaldehyde. Thus, the bands at 1635 cm^{-1} ($\nu(C=O)$), at 1609 cm^{-1} ($\nu(C=C)$), at 1270 cm^{-1} ($\delta(C–H)$) and at 1172 cm^{-1} ($\nu(CC)$), characteristic for crotonaldehyde (II), are the results of *β*-aldolization of acetaldehyde on the surfaces. The reduction of acetaldehyde (with the help of protons in the surface OH groups) to ethoxy (IV) caused the appearance of the bands at 2874 cm^{-1} ($\nu(CH)$) and at 1059 cm^{-1} ($\nu(CO)$).

The relevant shift down of the acetaldehyde C = O stretching from 1730 cm^{-1} (observed in the gas phase) to 1692 cm^{-1} suggests that part of acetaldehyde is adsorbed on Lewis sites through one of the oxygen lone pairs. The negative features at 3783, 3730 and 3680 cm^{-1}, as well as the broad absorptions centered at 3584–3570 cm^{-1} show that another part of acetaldehyde may adsorb through hydrogen bridge bonding with OH groups of the catalysts.

With the increase of acetaldehyde pressure to 1.33 hPa the intensities of the bands increased and shifts in the positions of some bands could be observed (figure 2). The band due to $\nu(C=O)$ of acetaldehyde became dominant and shifted upward (from 1692 to 1702 cm^{-1}) in 1.33 hPa. A downward shift (from 1391 to 1379 cm^{-1}) was observed in the position of $\delta(CH)$ band of acetaldehyde. At 1.33 hPa a new band at 1132 cm^{-1} due to $\nu(CC)$ of acetaldehyde could be detected. Most of the bands due to adsorbed crotonaldehyde ($\nu(C=O)$, $\nu(C=C)$, $\delta(CH)$) shifted to higher wavenumbers, while the 1172 cm^{-1} band ($\nu(CC)$ of crotonaldehyde) showed a downward shift to 1151 cm^{-1} with the increase of acetaldehyde pressure. New band at 1594 cm^{-1} (possibly due to $\nu(C=C)$ of crotonaldehyde) was developed, when the pressure was increased from 1.33 Pa to 1.33 hPa. Interestingly, the positions of the

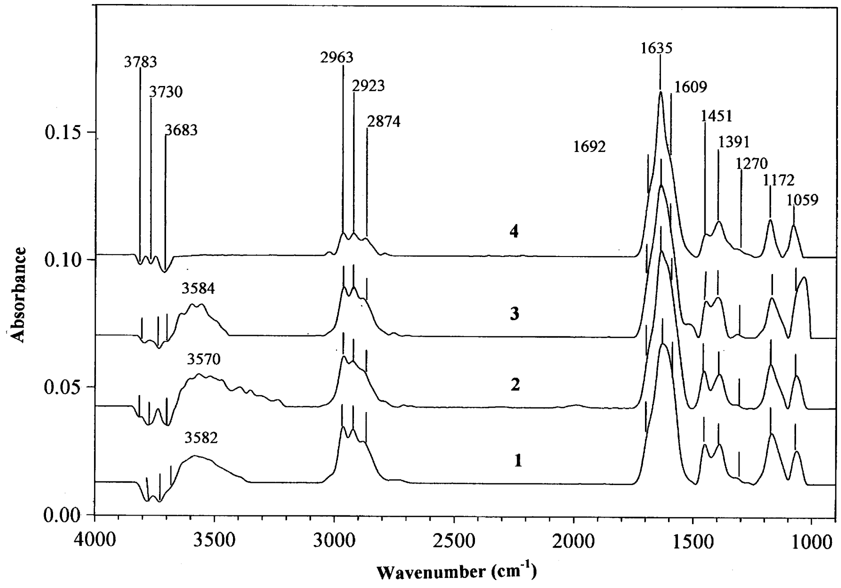

Figure 1. IR spectra registered at 300 K in the adsorption of 1.33 Pa acetaldehyde on reduced catalysts: 1 – Al_2O_3; 2 – 1% Rh/Al_2O_3; 3 – 1% Au/Al_2O_3 and 4 – 1% Pt/Al_2O_3. Adsorption time was 15 min.

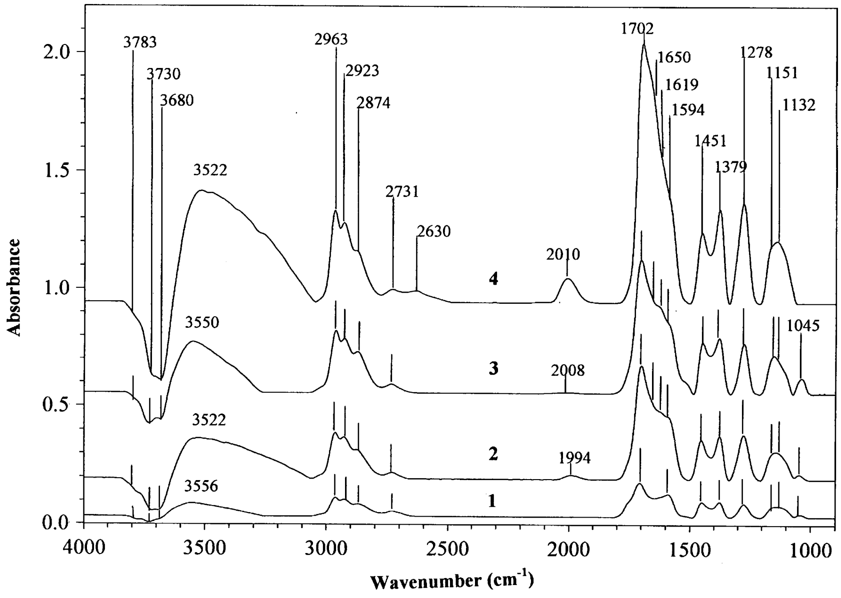

Figure 2. IR spectra registered at 300 K in the adsorption of 1.33 hPa acetaldehyde on reduced catalysts: 1 – Al_2O_3; 2 – 1% Rh/Al_2O_3; 3 – 1% Au/Al_2O_3 and 4 – 1% Pt/Al_2O_3. Adsorption time was 15 min.

negative features were unaltered, the centers of the broad absorptions, however, shifted to lower wavenumbers with the increase of acetaldehyde pressure. On the spectra of metal containing Al_2O_3 catalysts very small bands at 2010–1994 cm^{-1} became detectable, which are probably due to H-perturbed CO adsorbed on the metal sites.

In the next experiments the adsorbed acetaldehyde layer (produced by the adsorption of 1.33 hPa acetaldehyde at 300 K, 15 min and subsequent evacuation at 300 K for 5 min) was heated up during evacuation to different temperatures, kept at these temperatures for 1 min and cooled down to 300 K. The spectra developed by these treatments and registered at 300 K on 1% Pt/Al_2O_3 were collected in figure 3.

The intensities of the bands characteristic for C–H stretching vibrations in the range of 3000–2700 cm^{-1} continuously decreased with the increase of the temperature. Their traces, however, could be detected even after the treatment at 673 K. In the 1800–900 cm^{-1} range the bands at 1697 cm^{-1}(ν(C=O) of acetaldehyde), at 1382 cm^{-1} (δ(CH) of acetaldehyde) and at 1131 cm^{-1} (ν (C=C) of acetaldehyde), as well as the bands at 1604 cm^{-1} (ν(C=C) of crotonaldehyde), at 1284 cm^{-1} (δ (C—H) of crotonaldehyde) and at 1168 cm^{-1} (ν(CC) of crotonaldehyde) drastically decreased at 373 K; at and above 423 K the bands at 1697, 1614, 1382 and 1284 cm^{-1} were not observed. From 423 K new bands at 1564 cm^{-1} (possibly due to acetate) and at 1478 and 1350 cm^{-1} (tentatively assigned to carbonates) were detected, the intensities of which decreased with the further increase of the temperature. Spectral features due to hydrogen bridge bonding (not shown) were observed up to 523 K, after the treatment at 573 K and above these features disappeared from the spectra. The intensity of the 2010 cm^{-1} band showed a maximum at 373 K, it could be, however, detected even after the treatment at 673 K. Similar behavior of the bands were experienced on other noble metal containing catalysts. The spectral features due to H-bridge bonding disappeared already at 423 K and there was no band between 2100 and 2000 cm^{-1} on the spectra of pure Al_2O_3.

During the above treatments the desorbed molecules were analyzed by mass spectrometer. Data for the main products from different catalysts were collected on figures 4 and 5. Acetaldehyde desorption shows a maximum at about 400 K, however, the desorption of it was detected even above this temperature: on Al_2O_3 and on 1% Au/Al_2O_3 catalysts a second maximum at 600 K was also observed in molecular acetaldehyde desorption (figure 4a). These findings are in harmony with the IR data showing two forms of adsorbed molecular acetaldehyde on these surfaces.

According to IR data crotonaldehyde ($CH_3CH{=}CHCHO$) was produced by β-aldolization of acetaldehyde already at 300 K. Its desorption depicted a maximum at 400 K from all catalysts (figure 4b).

Among the desorption products benzene was detected with two maxima at 440 K and at 623 K (figure 4c). The formation of benzene has been formerly detected in the interaction of ethanol with Pt/CeO_2 [16] and it was interpreted as the formation of acetaldehyde (the product of dehydrogenation of ethanol), was followed by subsequent production of crotonaldehyde (the result of β-aldolization of acetaldehyde) and their reaction:

$$\begin{aligned} &CH_3CHO_{(a)} + CH_3CH{=}CHCHO_{(a)} \\ &\quad \rightarrow CH_3CH{=}CH{-}CH{=}CH{-}CHO_{(a)} + H_2O \end{aligned} \tag{1}$$

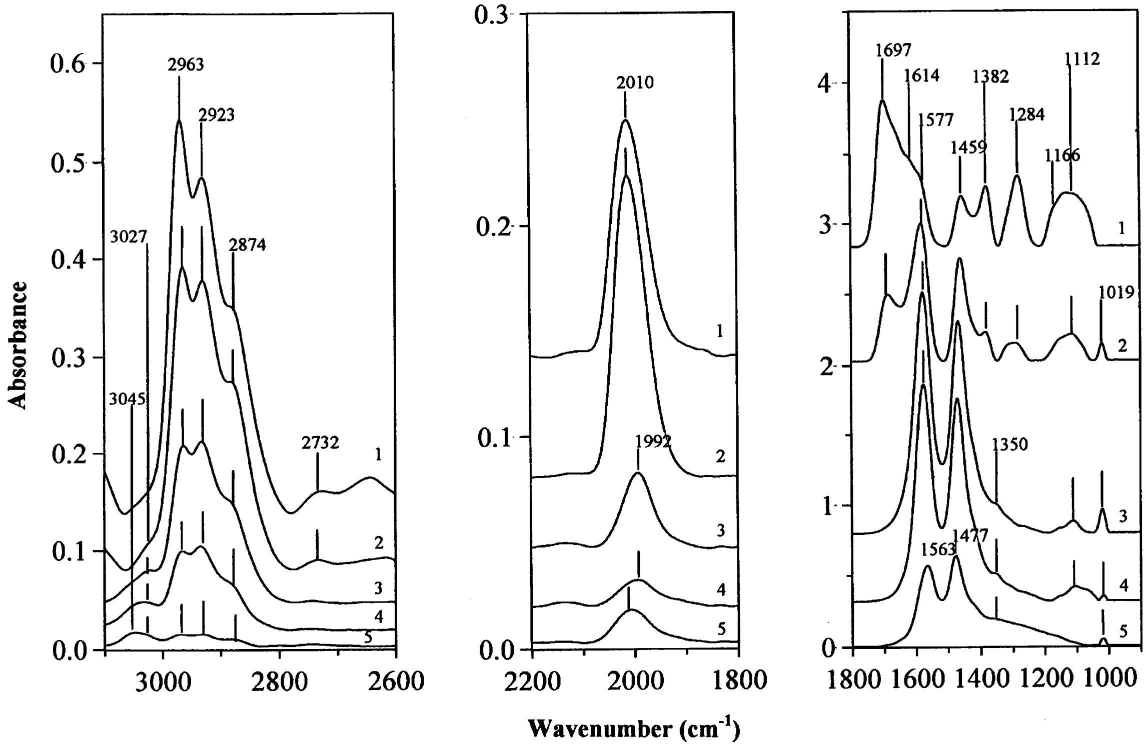

Figure 3. IR spectra taken at 300 K after different heat treatments in vacuum (see text) of adsorbed acetaldehyde layer on 1% Pt/Al_2O_3: 1 – 300 K; 2 373 K; 3 – 473 K; 4 – 573 K and 5 – 673 K.

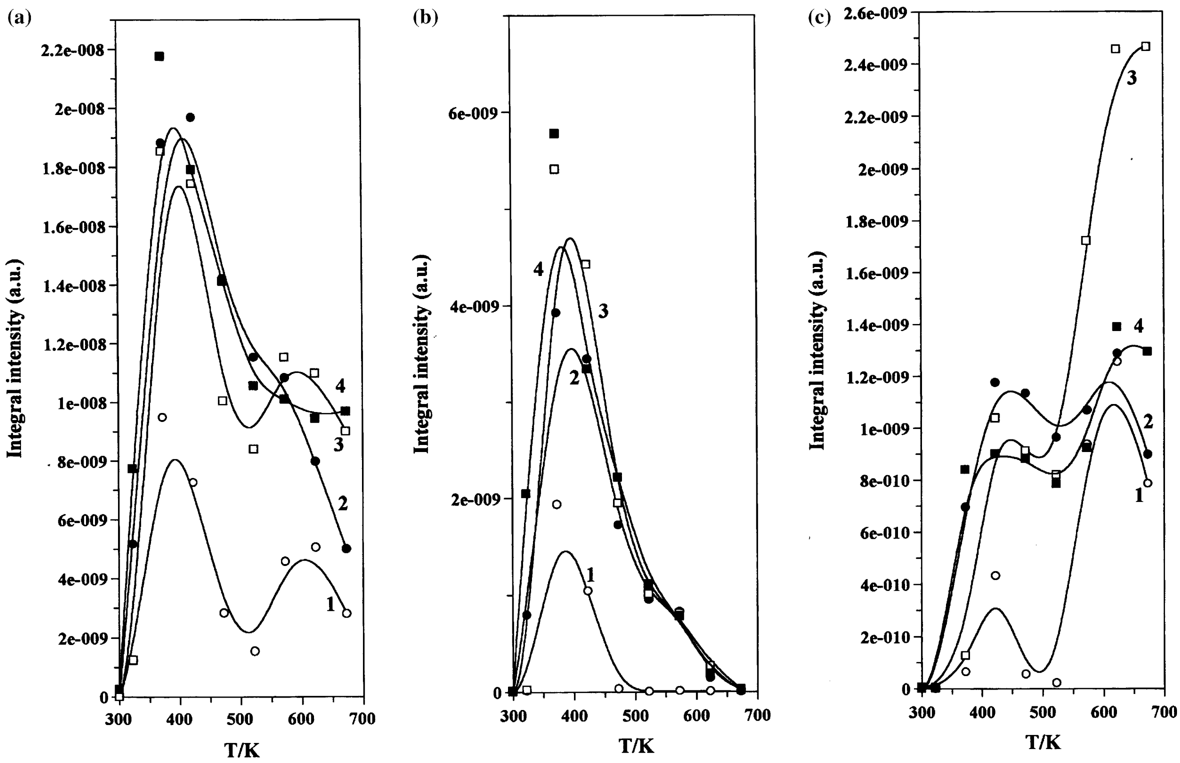

Figure 4. Formation of some gas phase products (monitored by MS) during the heat treatments (see text) of adsorbed acetaldehyde layer on reduced catalysts: 1 – Al_2O_3; 2 – 1% Rh/Al_2O_3; 3 – 1% Au/Al_2O_3 and 4 – 1% Pt/Al_2O_3. (a) acetaldehyde; (b) crotonaldehyde and (c) benzene.

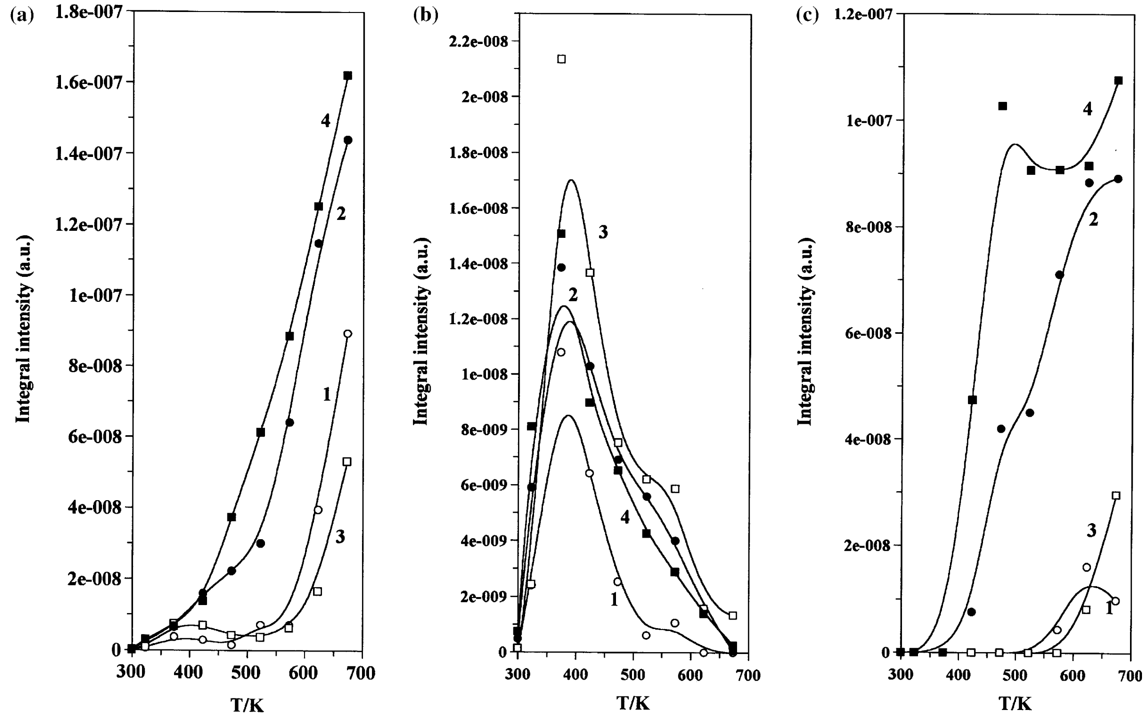

Figure 5. Formation of some gas phase products (monitored by MS) during the heat treatments (see text) of adsorbed acetaldehyde layer on reduced catalysts: 1 – Al_2O_3; 2 – 1% Rh/Al_2O_3; 3 – 1% Au/Al_2O_3 and 4 – 1% Pt/Al_2O_3. (a) hydrogen; (b) ethane and (c) ethylene.

resulting in 2,4-hexadienal and water. According to the explanation of [16] 2,4-hexadienal suffers a C–H bond dissociation of its methyl group on Pt, which after intramolecular cyclization followed by H_2O elimination may give benzene. The first maximum in benzene desorption corresponds well to that of acetaldehyde and crotonaldehyde desorption. The second benzene desorption maximum draws the attention to benzene formation possibly from the strongly held acetaldehyde (bonded to Lewis sites). The band at 3027 cm^{-1} detected at lower temperatures is tentatively assigned to adsorbed 2,4-hexadienal, while the 3045 cm^{-1} appearing at higher temperatures is tentatively due to adsorbed benzene (figures 1 and 2).

The strongly held acetaldehyde, on the other hand, may undergo decomposition processes. The appearance of H_2 in the gas phase (figure 5a) shows that dehydrogenation occurred above 423 K, at the temperature at which acetaldehyde, crotonaldehyde and benzene desorptions exhibited maximum. H_2 formation depended on the nature of the metal: the most effective metal was Pt; on 1% Pt/Al_2O_3 catalyst H_2 evolution started already at 423 K and its amount was the highest. Au/Al_2O_3 catalyst proved to be the least active, as H_2 started to evolve only at 573 K on this surface.

Ethane formation was detected from all surfaces investigated; T_{max} of its desorption appeared at about 400 K (figure 5b). The appearance of ethane as desorption product could be connected with the formation of adsorbed ethoxy (through the reduction of acetaldehyde with the help of protons in surface OH groups – figures 1 and 2) and the catalytic decomposition of ethanol [14], which could be produced from adsorbed ethoxy. The fact that ethanol was not detected in the gas phase from noble metal containing Al_2O_3 catalysts seems to strengthen the above explanation.

Above T_{max} of ethane desorption ethylene appeared among the gas phase products (figure 5c). We think that ethylene may be the product of ethane dehydrogenation; H_2 thus produced may contribute to H_2 formation in the dehydrogenation of strongly held acetaldehyde (see above).

Next the interaction of acetaldehyde with the reduced catalysts was investigated isothermally. In these experiments the samples were kept in 1.33 hPa acetaldehyde at 300, 373, 473 and 573 K for 60 min each. The IR spectra were recorded in time at the adsorption temperature and at the same time changes of the gas phase composition were monitored by mass spectrometer.

The IR spectra registered on 1% Rh/Al_2O_3 after 60 min adsorption at different temperatures were collected in figure 6.

In the ranges of 3100–2600 and 1800–900 cm^{-1}, respectively, all the bands assigned in connection with figures 1 and 2 appeared already in the first minute at 300 K. The bands of very small intensities at 2010 and 1966 cm^{-1} were detected at 300 K, which are tentatively assigned to H-perturbed CO adsorbed on metallic sites. The intensities of these bands increased only slightly in time at 300 K.

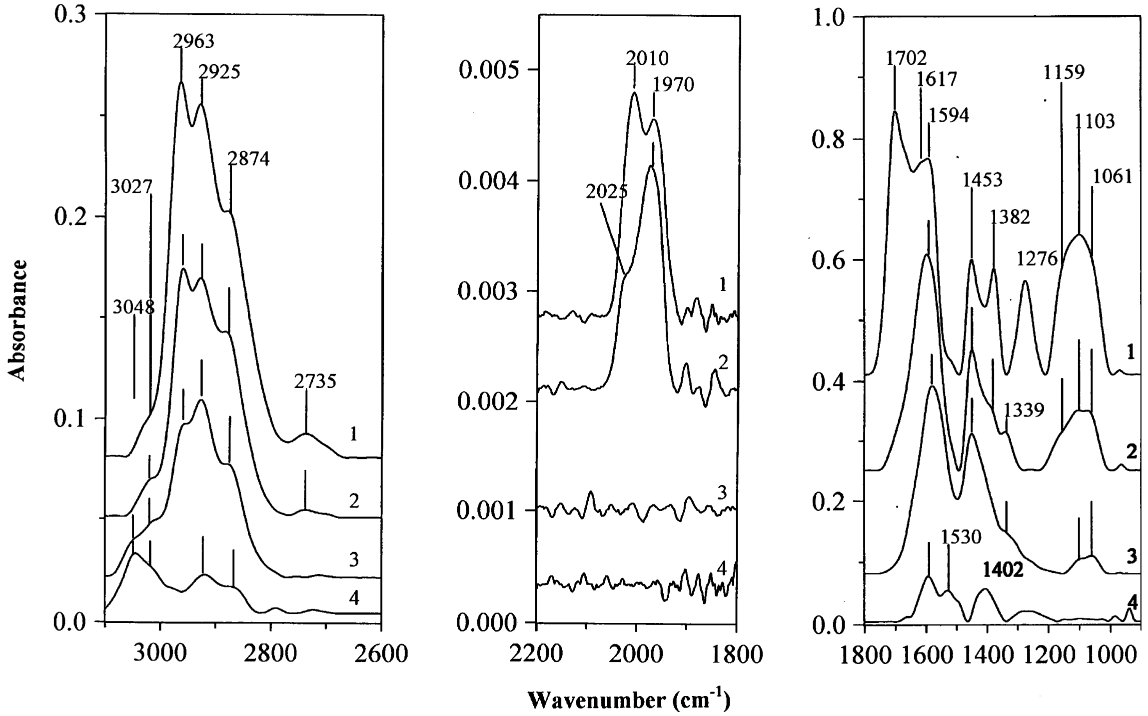

Figure 6. Infrared spectra registered in isotherm experiments after 60 min adsorption of 1.33 hPa acetaldehyde on reduced 1% Rh/Al_2O_3: 1 – 300 K; 2 – 373 K; 3 – 473 K and 4 – 573 K. The spectra were taken at the adsorption temperatures.

At 373 K the bands at 1702 cm^{-1} (ν(C=O) of acetaldehyde), at 1617 cm^{-1} ν(C=C) of crotonaldehyde) and at 1276 cm^{-1} (δ(C–H) of crotonaldehyde) appeared no more. The intensities of other bands were smaller at 373 K than at 300 K.

Dramatic changes occurred at and above 473 K: besides the overall decrease of the bands intensities, a new band at 3048 cm^{-1} (tentatively assigned to adsorbed benzene) appeared at 473 K, the bands in the 2200–1800 cm^{-1} range were not further observed, and in the range of 1800–900 cm^{-1} the bands due to acetate and carbonates became dominant.

Bands due to H-bridge bonded acetaldehyde could be observed at 300–473 K in isotherm experiments, at 573 K, however, they were not registered.

The gas phase composition was changed only at 473–573 K. The amount of acetaldehyde in the gas phase decreased only slightly on pure Al_2O_3 at 573 K, on noble metal containing catalysts, however, acetaldehyde practically disappeared from the gas phase in 60 min. The highest amount of crotonaldehyde formed in the interaction between Al_2O_3 and acetaldehyde at 573 K. Appreciable amount of crotonaldehyde was detected on 1% Rh/Al_2O_3, and there was practically no crotonaldehyde production on 1% Pt/Al_2O_3 and 1% Au/Al_2O_3. The effectiveness order of the catalysts in producing of benzene at 573 K seems to the opposite of their productivity of crotonaldehyde: the highest amount of benzene was found on 1% Au/Al_2O_3 and the amount of benzene decreased in the order of 1% Au/Al_2O_3 > 1% Pt/Al_2O_3 > 1% Rh/Al_2O_3 > Al_2O_3.

The amount of H_2 evolved at 573 K was also depended on the nature of the metal: the highest amount of H_2 was produced on 1% Pt/Al_2O_3, and the effectiveness of the catalysts in forming of H_2 decreased in the order of 1% Pt/Al_2O_3 > 1% Rh/Al_2O_3 > 1% Au/Al_2O_3 > Al_2O_3. Ethane formation depended on the temperature and on the nature of the metal. The amount of ethane decreased with the increase of the temperature. On 1% Rh/Al_2O_3 there was no ethane formation at 573 K. The highest amount of ethane was detected on pure Al_2O_3 at 573 K, small amount of ethane was measured on 1% Au/Al_2O_3 and 1% Pt/Al_2O_3.

Interestingly, ethylene was not detected among the gas phase products at 300–573 K in isotherm experiments. Instead of ethylene, small amount of acetylene was detected, as the possible product of ethane dehydrogenation. The amount of acetylene changed parallel with that of ethane as a function of temperature and that of the nature of the metals.

4. Conclusions

1. Acetaldehyde adsorbs molecularly on Al_2O_3-supported noble metal catalysts through the protons of surface OH groups forming H-bridge bonding and/or through one of its oxygen lone pairs on surface Lewis sites.
2. Acetaldehyde transforms by β-aldolization into crotonaldehyde; this transformation depends on the temperature and on the nature of the metal.

3. At higher temperatures benzene formed via the reaction of acetaldehyde and crotonaldehyde, as well as the dehydrogenation of more stable acetaldehyde proceeded. All these surface processes depended on the nature of the metal.

Acknowledgments

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