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The various types of acetaldehyde adsorption on clean, and on modified Rh(111) surface

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Abstract: Rhodium is an effective catalyst in the CO+H_2 reaction into C_2-oxygenates. Among the products, acetaldehyde (AA) is an important hydrogen carrier which is also produced in the decomposition of ethanol on metal surfaces. The interaction of CH_3CHO with Rh(111) surface has been investigated by AES, EELS, TDS and $\Delta\Phi$ methods. The chemisorbed acetaldehyde starts to decompose at 200 K. The main products of the chemisorbed AA are CO and CH_4. Minor products are adsorbed H and C. In the chemisorbed layer η_1-(O)-CH_3CHO_a and η_2-(O,C)-CH_3CHO_a have been observed. Electronegative and electro positive modifiers may influence the stability of these surface complexes such as i.) surface C_a acts as a simple contaminant by site blocking mechanism. ii) a direct surface reaction with O_a led to the formation of acetate. iii) K_a increases the thermal stability of acetaldehyde by an extended electronic interaction.

Keywords: CO_2; oligomerization; thermal desorption; alkali promotor;

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1. Introduction

Aldehydes are gas-phase products of the decomposition of primary alcohols on metal surfaces [1-2]. Acetaldehyde has an environmental risk because of its carcinogen effect [3]. On the other hand, AA as an intermediate or end product can be a good candidate for chemical energy storage; as a more valuable product of COx hydrogenation [4]. In the ethanol steam reforming reaction the H_2 could release for fuel cell applications. [5]. Transformation of AA into paraldehyde $(CH_3CHO)_3$ enables to use this couple of compounds in heat pumps [6].

2. Materials and Methods

For our experiments the Rh single crystal from Materials Research Corporation (purity 99,99 %) was cut with (111) orientation. After inserting into the UHV chamber it was sputtered with Ar+ ions. (Typically 1kV, $1x10^{-7}$ mbar and 2mA for 10-30 min.) and finally it was heated to 900-1100K and this was repeated until no contamination was detected by AES. Two UHV chamber were used for the TDS and HREELS measurements. The crystal was cooled to 100 K and 150 K for TDS and HREELS measurements, respectively.

Acetaldehyde (CH_3CHO) of 99% purity was purchased from Sigma-Aldrich and it was purified by several freeze-pump-thaw cycles and for adsorption it was dosed through a capillary which was placed 1.5 cm from the sample.

Oxygen (from Messer-Griesheim, 99,99% purity) was used for cleaning after each desorption through a second capillary. A SAES type potassium source was used - after several minutes degassing - for K atom evaporation.

The first UHV system for mainly TDS experiment with a base pressure of $5x10^{-10}$ mbar, was described previously [7-9]. It was also used for AES, ELS, work function ($\Delta\Phi$) and TDS measurements. A VG mass spectrometer which was placed ca. 1 cm from the single crystal. For TDS 5 K/s heating rate was chosen. The ELS (in the electronic range) were taken by means of a cylindrical mirror analyzer (PHI). The low energy cut off in the ELS was used for $\Delta\Phi$.

3. Results

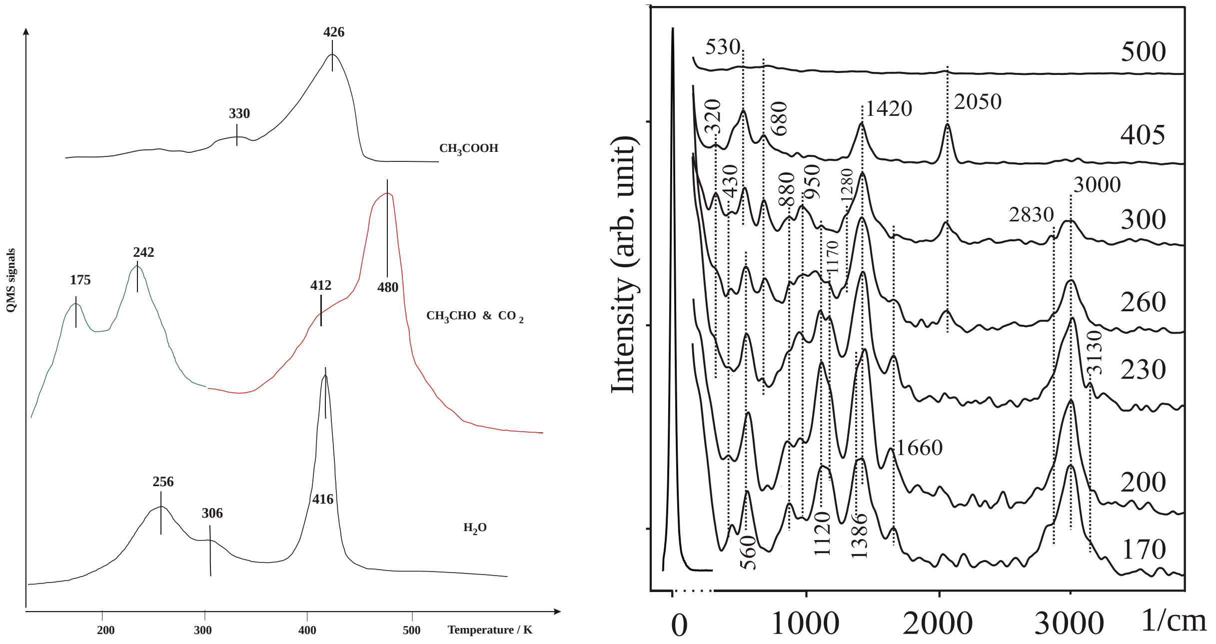
3.1. Reaction on clean and carbon contaminated Rh(111)

The decomposition of AA on clean rodium has been studied in details previously by AES, EELS, TDS and work function methods [10]. Nevertheless, we give a short summary -as a starting point- about those results here as well. The chemisorbed acetaldehyde started to decompose at 200 K producing mainly adsorbed CO and CH_4 which desorbed at Tp=260K. Minor products were adsorbed H and C, too. A weakly adsorbed CH_3CHO desorbed in a sharp peak centered at 150 K. Oligomerised acetaldehyde was also found ($[CH3CHO]_n^+$, $1<n<5$) in the gase phase with Tp=225-235 K. The low temperature state was monomer while we observed oligomers namely paraldehyde. On the carbon contaminated surface our HREELS measurements confirmed also the presence of η_1-(O)-CH_3CHO_a and η_2-(O,C)-CH_3CHO_a in the chemisorbed layer. Carbon contamination has a site blocking effect on the adsorption of AA from the gas phase. The amount of products like CH_4, oligomers decreased rapidly with a small shift in Tp values. This effect is less pronounced in the case of CO desorption and at the same time hydrogen desorption suggests the presence of some CxHy moties.

3.2. Reaction with oxygen precovered Rh(111)

The preadsorbed oxygen changed the product distribution, and new products, like water, CO_2 and acetic acid could be detected in TDS (Figure 1A). Water desorbed in a sharp peak, with Tp= 416 K. Two minor peaks centered at 256 K and 306 K also appeared. By recording the CO_2 desorption at amu 44 one can see the evaluation of acetaldehyde as well, since it has a contribution at that mass number too. The higher temperature peaks, with Tp=412 K and 480 K can be considered as CO_2 (red line) and the peaks at Tp=175 K and 242 K as CH_3CHO (green line). The desorption at mass 60 is connected to CH_3COOH with peaks at Tp= 330 K and 420 K.

Based on our HREELS results, we observed the formation of acetate as an intermediate, which is indicated by the appearance of ν_a(OCO) vibration in the spectra at 1660 cm^{-1} (Figure 1b). In addition, an increase in the thermal stability of acetate (up to T = 325 K) was also observed with increasing oxygen coverage (not shown).

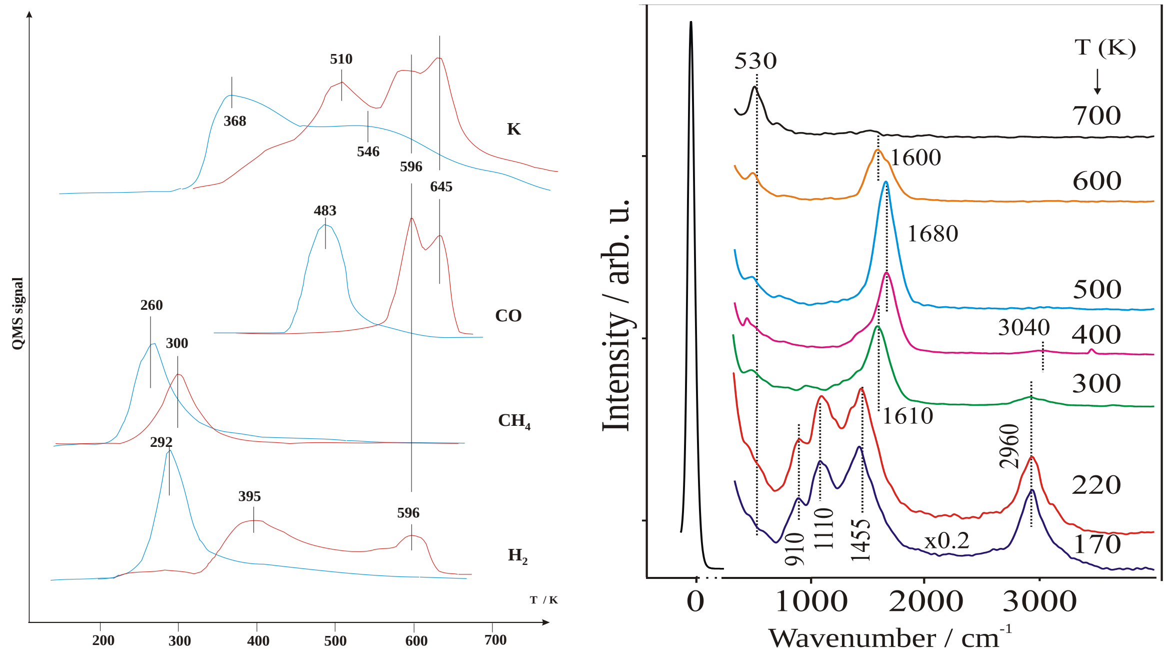


(**a**) (**b**)

Figure 1. (**a**) Selected TDS spectra from the CH_3CHO + Oa layer on Rh(111). The products of H_2O, $CH_3CHO+CO_2$ and CH_3COOH has been detected at amu= 18, 44 and 60 respectively. (**b**) HREELS spectra collected from the oxygen preadsorbed (0.25 ML) Rh(111) surface after exposed to 10 L of acetaldehyde at 170 K, and subsequent annealing to higher temperatures.

3.3. The effect of potassium on the adsorption of AA on Rh(111)

The preadsorbed K atoms dramaticaly changed the stability of adsorbed molecules and its desorption products. Figure 2A shows the products from clean Rh(111) (blue line) compared to their desorption from the monolayer K covered surface. The hydrogen desorption from clean surface presented at Tp=292 K was transferred to 395 K and 596 K. Methane desorption suffered only a minor shift, from 260 K to 300 K. CO desorption from clean surface at 483 K was pulled to 596 K and 645 K. The K desorption curves represent its desorption from bare Rh(111) (blue line) and from the coadsorbed layer (red line). The broad features at Tp= 368 K and 546 K was shifted to 510 K, 596 K and 645 K. Here we have to point out the coincidence peaks centered at 596 K in the case of H_2, CO and K desorption . As a result of the increased electron concentration, the amount of adsorbed material increased and a surface complex formed between potassium and the decomposition intermediates of acetaldehyde. This is also indicated by the significant shift and stability of the ν(C-O) valence vibration on the HREEL spectra due to the interaction with potassium (Figure 2b). The peaks at 1810-2100 cm^{-1} , which are characteristic of the CO adsorption on the pure rhodium surface depending on the adsorption center, were significantly shifted in that case together with the desorption temperatures of the decomposition products.



(**a**) (**b**)

Figure 2. (**a**) Thermal desorption spectra of H_2, CO and CH_4 from the AA covered (blue line) and with K coadsorbed (red line) layer. The two spectra at amu=39 represent the K TDS without AA (blue line) and with AA coadsorbed layers. (**b**) Effect of potassium (0.13 ML) on the HREEL spectra after adsorption of 10 L of acetaldehyde on Rh(111), T_a= 170 K.

4. Discussion

4.1. The reaction with preadsorbed O compared to bare and carbon contaminated layer

The product distribution also reflects the fact that partially and fully oxidized processes took place on the surface.. Some of the original AA molecules must have decomposed. Not only C-H bonds were broken, giving H_a atoms on the surface but C-C bond ruptured as well. The latter makes CO_2 desorption possible. The fact that its peak temperature is the highest supports the the oxidation of surface carbon. The acetic acid desorption nearly identical with the one after direct CH_3COOH adsorption (not shown).

4.2. The effect of K atoms on the reaction routes

Surface potassium has a very strong stabilisation effect on the surface layer. The different products appeared at significantly higher temperatures, these shifts were as large as 40 - 300 K. The decomposition mechanisms must have changed too. The coincidence Tp values suggest the decomposition of a common state. To the interpretation of this finding we can reffer the similarties with our previos studies [8,9]. The K atoms donate electrons to the underlaying surface and to the adsorbed molecules. The electron distribution in the molecule might have changed and therefore it will influence the stability of η_1-(O)-CH_3CHO_a and η_2-(O,C)-CH_3CHO_a forms.

Author Contributions: All authors contributed equally to this paper as well as they have read and agreed to the published version of the manuscript.

Conflicts of Interest: The Authors declare there is no conflict of interest.

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