Modeling the surface chemistry of biomass-derived molecules on oxygen-covered Rh(100)

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SUPPLEMENTARY INFORMATION

Ethanol decomposition on the oxygen-free Rh(100) surface

Ethanol decomposition on the oxygen-free Rh(100) surface was studied by infrared spectroscopy and Density Functional Theory (DFT) to identify stable surface intermediates along the ethoxy decomposition pathway. Figure S1 shows infrared spectra obtained after 0.07 ML of ethanol adsorption at 100 K and subsequent annealing. The spectrum at 100 K shows no O-H stretching bands at 3500-3000 cm^{-1}. Two possible explanations for the lack of the O-H stretching mode in this coverage regime are either the orientation of the O-H bond parallel to the surface or by ethoxy (CH_3CH_2O) formation upon ethanol adsorption. In order to determine whether ethoxy formation occurs upon ethanol adsorption at 100 K and to follow the further decomposition steps after annealing, the reaction sequence of ethanol decomposition on Rh(100) was studied by density functional theory (DFT).

Periodic DFT computations were performed using the VASP package with plane wave (PW) basis sets and an RPBE functional. The cut-off energy used was 400 eV. Necessary dipole corrections due to the asymmetric usage of slabs were included into the computations. The Rh(100) surface was modeled with a 5-layer slab to describe the p(2x2) unit cell, corresponding to a surface coverage of 0.25ML for all species, where the repeating slabs were separated with a 12Å vacuum in Z-direction. During the simulations the bottom 3 layers were kept frozen. The remaining top 2 layers and the adsorbed molecules were relaxed until the net force acting on the ions was < 0.015 eV/Å. The reaction paths were generated using the climbing image (CI-NEB) method.
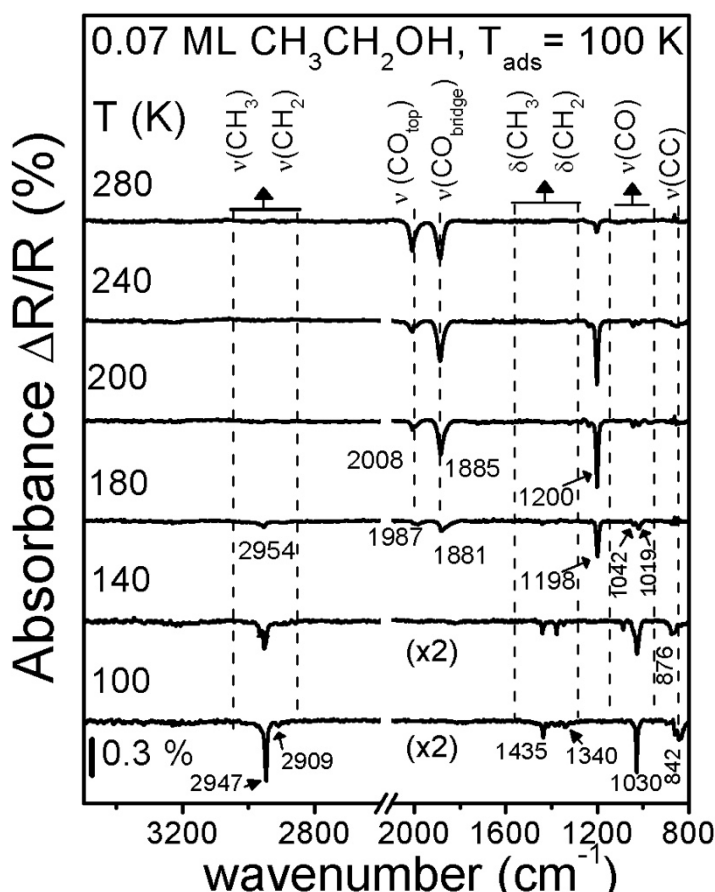
Figure S1. Temperature-programmed infrared spectroscopy (TP-IR) spectra of 0.07 ML ethanol adsorbed on Rh(100) at 100 K. The surface was heated stepwise and spectra were recorded at the temperatures indicated.

DFT computations show that ethanol can only adsorb dissociatively on the Rh(100) surface in the form of ethoxy. This process is exothermic by 16 kJ/mol. Figure S2 (middle picture) shows the most stable configuration, where both ethoxy and hydrogen occupy the bridge sites.

After heating to 180 K, the intensity of the ethoxy-related bands decreases substantially, as a result of ethoxy decomposition. Concurrently, new vibrational bands appear at 1987, 1881 and 1198 cm^{-1}, along with a band at 1042 cm^{-1} with a weak intensity. The bands at 1987 and 1881 cm^{-1} are assigned to the C-O stretching bands of molecular carbon monoxide occupying top and bridge sites, respectively. The appearance of CO-related bands concurrent with the intensity loss of ethoxy-related bands suggests that ethoxy decomposes to CO via C-H and C-C bond scissions.

The bands at 1198 and 1042 cm^{-1} lose most of their intensity after heating to 280 K, which is accompanied by an increase in the intensity of the CO-related bands (Figure S1). This suggests that the species, which is responsible for the presence of the band at 1198 and 1042 cm^{-1} release CO on the surface. In other words, this species contains a -CO- group in its structure. The band at 1042 cm^{-1} shows a similar intensity change with the 1198 cm^{-1} band as a function of temperature (Figure S1), suggesting that these two bands are related to the same species. In

order to identify this surface species DFT simulations were performed for a number of OCH_xCH_y type surface intermediates. Among these, the proposed oxometallacycle (OCH_2CH_2) intermediate (Figure S2-bottom picture) produces the 1204 cm⁻¹ and 1043 cm⁻¹ bands, which are assigned to the CH_2 twisting and the C-C stretching modes of the oxometallacycle, respectively. The good agreement between the theoretical and experimental results indicates that the oxometallacycle is a surface intermediate for ethoxy decomposition at low coverage.
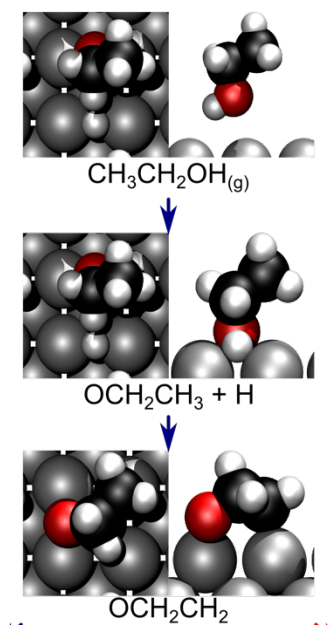

CH₃CH₂OH₍g₎

OCH₂CH₃ + H

OCH₂CH₂

Figure S2. Energetically favorable pathways for the decomposition of ethanol on Rh(100).

Acetic Acid Decomposition on Rh(100)

Acetic acid decomposition at low coverage was first studied by TPRS. The desorption spectra of 0.05 ML (ca. 1/5 saturation coverage) acetic acid show H_2 (362 and 450 K) and CO_2 (356 K) desorption, along with a small amount of CO (505 K) (Figure S3(a)). CO_2 evolution at 356 K coincides with the first H_2 desorption peak (at 362 K), indicative for acetate decarboxylation [3, 4]. Consistent with this, TP-IR results shown in Figure S3(b) confirm this assignment. After adsorption at 100 K followed by heating to 180 K the surface is covered by acetate, characterized by the band at 1416 cm⁻¹, which is assigned to the symmetric O-C-O stretching mode of acetate. In addition, minor CO related bands appear at 1982 (CO top) and 1855 cm⁻¹ (CO bridge) after heating to 180 K, suggesting that a small portion of acetate decomposes to CO via C-O and C-C bond scissions. The acetate-related bands disappear when heated, and after heating to 360 K they have completely disappeared.

As acetate decomposes, it releases CO_2 and CH_x ad-species on the surface. The resulting CH_x species can either hydrogenate to methane or dehydrogenate to surface carbon. The lack of methane evolution and the observed surface carbon identified by a subsequent TPO experiment indicate that the dehydrogenation pathway dominates. The H_2 desorption peak at 450 K is attributed to dehydrogenation of CH_x species.
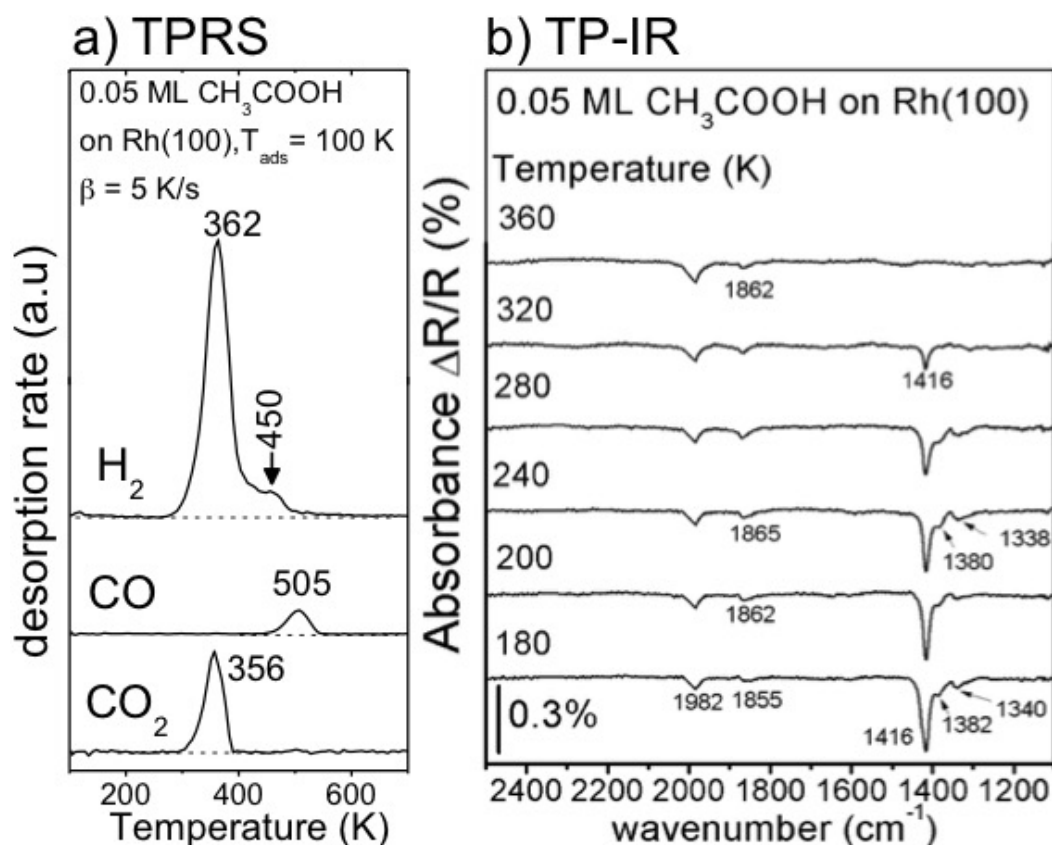
Figure S3. a) TPRS spectra obtained after 0.05 ML acetic acid adsorbed b) TP-IR spectra of 0.05 ML acetic acid adsorbed at 100 K and after subsequent annealing. The surface was heated stepwise and spectra were recorded at the temperatures indicated.

References

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