The effect of C-OH functionality on the Surface Chemistry of Sugars: Ethanol Chemistry on Rh(100)

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SUPPLEMENTARY INFORMATION

Acetaldehyde Decomposition on Rh(100)

Acetaldehyde decomposition at saturation coverage (0.25 ML) was investigated by using TPRS and RAIRS. TPRS was used to monitor the thermal decomposition products after 0.25 ML acetaldehyde adsorption and following annealing to 700 K. Fig. S1 shows that H_2, CH_4 and CO are the decomposition products. In addition, TPO showed the presence of surface carbon at the end of the TPRS run (not shown). The peak areas in TPRS and TPO spectra were used to quantify the decomposition products. Table S1 shows that at saturation coverage (0.25 ML), 60% of acetaldehyde (0.15 ML) decomposes to yield methane and CO, while the remaining 40% (0.10 ML) decomposes to hydrogen, CO and surface carbon. Methane forms due to the reaction between CH_x species and hydrogen.

Decomposition pathways and surface intermediates were analyzed by temperature programmed infrared spectroscopy (TP-IR). Fig. S2 shows the infrared spectra following 0.25 ML (saturation coverage) of acetaldehyde adsorption and subsequent heating. The acetaldehyde related bands at 1343 and 1072 cm^{-1} persist up to 240 K. Decomposition starts above 180 K, as evidenced by a dramatic increase in intensities of the CO related bands at 2050-2000 cm^{-1} (CO on top site) and 1950-1900 cm^{-1} (CO on bridge site) shown in Figure A.2- inset, and is complete at 280 K, where acetaldehyde related bands disappear completely. CH_4 and H_2 desorption at 250-300 K (Fig. S1) as a result of acetaldehyde decomposition is consistent with the infrared results. Hydrogen desorption causes a site change of CO from bridge to top, which is seen in the inset of the Fig. S2 after 280 K. The disappearance of CO related band is accompanied by CO desorption at 480 K.

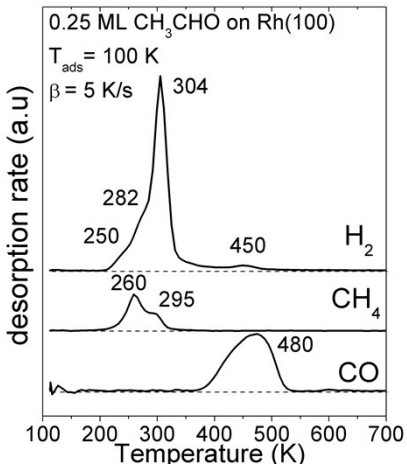

Fig. S1 TPRS spectra obtained after saturation coverage (0.25 ML) of acetaldehyde adsorption on Rh(100) at 100 K and subsequent heating. The heating rate is 5 K/s.

Table S1 TPRS and TPO yields of saturation coverage of acetaldehyde on Rh(100).

Coverage(ML)	TPRS and TPO Yields (ML)			
	CO	H_2	CH_4	C
0.25 (sat)	0.25	0.20	0.15	0.10

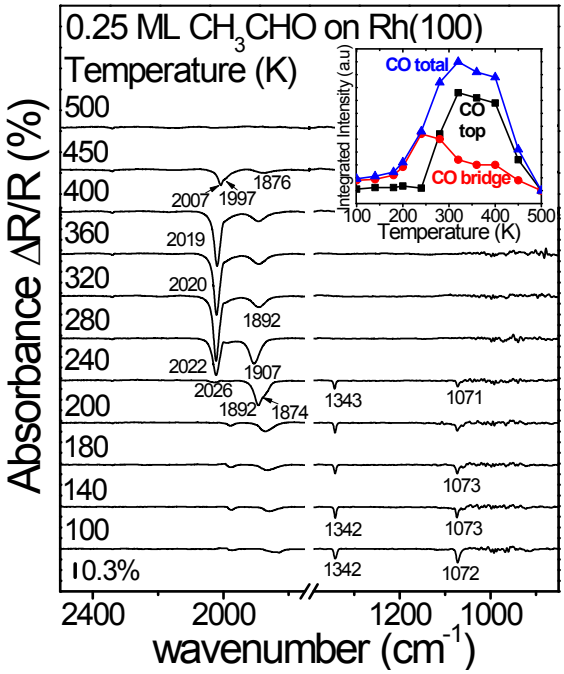

Fig. S2 TP-IR spectra of 0.25 ML acetaldehyde adsorbed at 100 K. The surface was heated stepwise with a rate of 1 K/s and spectra were recorded at the temperatures indicated.

Ethanol Decomposition at high coverage – Work Function Measurements

Work function measurements were performed to monitor changes on the surface during ethanol decomposition. Figure S.3 shows the work function change and desorption products during heating after after dosing a low and high quantity ethanol to the surface. Ethanol was dosed to the surface at 100 K and the surface was heated up to 650 K with 1 K/s. The coverage of ethanol was determined by TPRS data. Upon dosing 0.07 and 0.22 ML (saturation coverage) ethanol, the work function decreases by 0.75 and 1.9 eV, respectively. Infrared and DFT studies reported in the main text show that ethanol adsorbs dissociatively to form ethoxy. Ethoxy decomposition via dehydrogenation and C-C bond breaking occurs between 180-280 K, which causes a work function increase. As a result of decomposition, the work function is larger than the clean surface value due to the formation of CO, CH_x and H species. After annealing to 280 K, the work function decreases due to H_2 desorption. CO desorption, occurring around 490 K, results in a further work function decrease. The final work function value at 650 K is higher than the clean surface value due to the presence of surface carbon. Surface carbon formed as a result of 0.07 and 0.22 ML ethanol decomposition gives rise to 0.035 and 0.09 eV work function increase. Based on the linear relationship between coverage and work function change, these values correspond to 0.07 and 0.18 ML surface carbon. These values are the similar to the ones obtained from TPRS data.

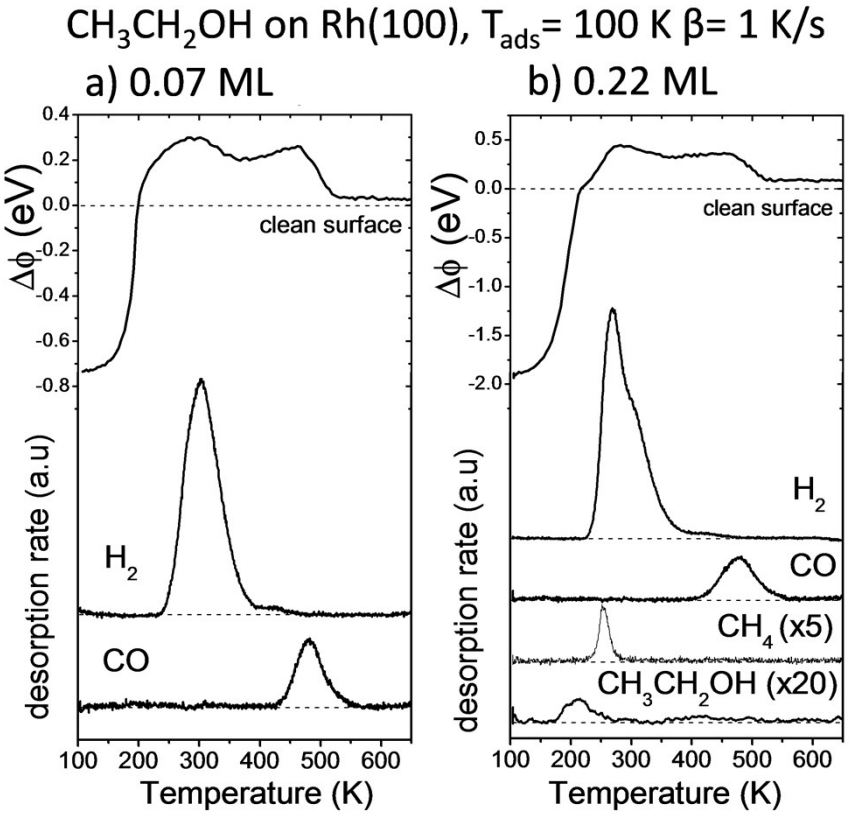

Fig. S3 Temperature programmed work function measurement and TPD spectra obtained after 0.07 ML (a) and 0.22 ML (b) ethanol adsorption at 100 K and subsequent annealing to 650 K. Heating rate is 1 K/s.