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Step enhanced dehydrogenation of ethanol on Rh

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ABSTRACT

We have investigated the adsorption and decomposition of ethanol on the Rh(111) and Rh(553) surfaces at room temperature with special emphasis on the dehydrogenation. We use high resolution core level photoemission and density functional theory (DFT) based simulations. A detailed analysis of the C1s core level spectra, including analysis of the vibrational fine-structure and comparison to calculated C1s binding energy shifts, shows that the ethanol decomposes into CO, ethylidyne (C_2H_3), methylidyne (CH), atomic C, and hydrogen. At low ethanol exposures, CH is the dominating hydrocarbon fragment on Rh(111), whereas on Rh(553) atomic C dominates over CH, indicating an enhanced dehydrogenation due to the steps present on the latter surface. At higher ethanol exposures we find a similar behavior of atomic C dominating over hydrocarbons on Rh(553), while on Rh(111) atomic carbon remains a minority species. Our DFT based simulations show that the enhanced dehydrogenation results from a significant lowering of the CH dissociation barrier from Rh(111) to Rh(553), as well as from the dissociation changing from endothermic on Rh(111) to exothermic on Rh(553).

1. Introduction

Hydrogen is being considered as a possible major energy source for the future, to be used in fuel cells where the hydrogen is oxidized into H_2O and electricity is produced. Storage of pure hydrogen, however, presents severe safety-related problems and it has therefore been suggested to store and transport the hydrogen in the form of a more stable hydrogen-containing compound from which the hydrogen is extracted in close proximity to its use in e.g. fuel cells. One such H-containing compound under consideration is ethanol, for which it has recently [1–4] been demonstrated that Rh-ceria based catalytic extraction of hydrogen by partial oxidation is possible at relatively low temperatures.

However, little is known about the reasons for the efficiency of the Rh-ceria based catalysts used for H_2 production. This applies not only to the partial-oxidation reaction but even to the fundamental steps of ethanol adsorption [5] and fragmentation on Rh surfaces. As edges and corners constitute a significant fraction of the surface area in the small Rh particles typically used in real catalysts, it is important to investigate what influence the presence of under-coordinated Rh atoms has on ethanol adsorption and fragmentation. We have therefore studied the room temperature adsorption and decomposition of ethanol on both the flat Rh(111) and the vicinal Rh(553) surfaces where the steps on the latter are used to mimic, at least partly, the under-coordinated atoms present at the edges and corners of small Rh particles. Our results show significantly different fragmentation of ethanol on these two surfaces, demonstrating a large influence of the under-coordinated step atoms at the 111-type microfacets of the Rh(553) surface. On both surfaces, we find that predominantly the C–C as opposed to the C–O bond of the ethanol molecule is broken due to the interaction with Rh. However, on the flat Rh(111) surface, hydrocarbons constitute a large fraction of the final decomposition products indicating non-complete dehydrogenation whereas on Rh(553) an atomic carbon species is found to dominate over hydrocarbon fragments indicating a more complete dehydrogenation at the steps. The enhanced dehydrogenation at the steps is shown to be the result of both a significantly lower energy barrier for CH dissociation as well as the dehydrogenation becoming exothermic at the steps.

In addition to providing information on ethanol adsorption and decomposition on Rh(111) and Rh(553), the present study also demonstrates the potential of high resolution core level spectroscopy (HRCLS) for identifying hydrocarbon fragments on surfaces. This potential, which is not restricted to the current Rh surfaces, rests on a detailed analysis of the vibrational fine structure present in the HRCLS C1s spectra of adsorbed hydrocarbons and on

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comparison to theoretical simulations of adsorption structures and C1s binding energy shifts [6–9].

2. Experimental and calculational details

The measurements were performed at beam line I311 at the synchrotron radiation facility MAX II in Lund, Sweden. We refer the reader to Ref. [10] for a detailed description of this beam line. Experimental procedures were as described in Ref. [11]. In short, the surfaces were cleaned by a combination of Ar^+ sputtering and annealing in O_2 and in vacuum. The surface cleanliness was checked by HRCLS and the long range order by low energy electron diffraction (LEED). The HRCL spectra were recorded at normal emission and at liquid nitrogen temperatures in order to reduce thermal broadenings. Special attention was paid to the possibility of beam induced dissociation due to the high incident flux. No such effects were found for the present experimental conditions.

Ethanol exposures are given in Langmuir (L) ($1\ L = 10^{-6}$ torr s) based on the gauge reading with no correction applied for the sensitivity towards ethanol [12]. Ethanol pressures in the low 10^{-8} torr range were typically used except for the lowest exposures. The ethanol was 99.5% pure with dry residuals less than 0.002% and was further purified by freeze-pump-thaw cycles.

The HRCL spectra were decomposed using Doniach–Sunjic line shapes [13] convoluted with Gaussian functions that represent unresolved vibrations and the experimental broadening. A linear background was included in the fits. For the case of hydrocarbons, it has long been known [14] that intrinsic excitation of C–H stretch vibrations in the photoemission process gives rise to higher binding energy satellites in the C1s spectra also for the case of chemisorbed molecules, see e.g. Refs. [6–9]. The energy separation of the C–H vibrational satellites is in all cases close to 400 meV and the intensity distribution closely follows a Poisson distribution as expected from a linear coupling model [15]. For the decomposition of hydrocarbon spectra we have therefore used vibrational components with an energy splitting of close to 400 meV and the additional constraint that the intensities of these components follow a Poisson distribution.

For the slab-based calculations of surface structures we used density functional theory (DFT) as implemented in the DACAPO package [16]. Ion-cores were described by ultrasoft pseudopotentials [17]. In order to describe core ionized C atoms, we used a pseudopotential constructed for a C atom where a 1s electron had been promoted to a 2p valence level [18–21]. The one-electron wave functions were expanded in a plane wave basis with an energy cutoff of 25 Ry. For the exchange and correlation functional we used the generalized gradient approximation (GGA) as implemented in the PW91 form [22]. For Rh(111) we used a three-layer slab and for Rh(553) a slab containing three (111) Rh layers. The first two substrate layers as well as the adsorbates were allowed to relax geometrically. The slabs were separated by vacuum layers of thickness equivalent to five (111) Rh layers. Energy barriers were found by constrained relaxation with care being taken that the pathways become continuous. Sampling of k-space was done using a $(2 \times 4 \times 1)$ mesh for the (5×2) and (1×2) unit cells used for Rh(111) and Rh(553), respectively. The theoretical lattice constant 3.83 Å was used for Rh. Finally, the C1s core level binding energy shifts were calculated as total energy differences between systems where the appropriate C-atoms had been core-ionized. Convergence tests showed that increasing the slab thickness from three to five layers caused the relative differences of the adsorption energies for atomic C and CH at different sites to change by less than 50 meV. Changes of the corresponding C1s core level shifts were less than 10 meV. The conclusions based on three layer slabs are therefore not affected.

3. Results and discussion

C1s spectra measured after representative room temperature ethanol exposures ranging from 0.1 to 30 L on Rh(111) and Rh(553) are shown in Fig. 1a and b, respectively, together with decompositions into a number of components.

3.1. C1s results, overview

The C1s peaks at binding energies above 285 eV can all be assigned to CO molecules adsorbed in different sites on the two surfaces. For Rh(111) the components at ~286 and ~285.4 eV are assigned to CO molecules in on-top and three-fold-hollow adsorption sites, respectively, based upon their binding energies, as discussed in more detail in [11]. The shoulder at ~286.3 eV on the high binding energy side of the on-top peak is due to the intrinsic excitation of the C–O stretch vibration in the photoemission process [23] and not to CO in a different configuration. For Rh(553), the C1s components at similar binding energies as those found on Rh(111) are interpreted as due to CO molecules in on-top and three-fold-hollow sites on the (111) terraces of the surface. In addition, a C1s component at ~285.7 eV is clearly visible after ethanol exposures up to 1 L. This component can, by comparison to C1s spectra measured after CO exposure of Rh(553) [24], be ascribed to CO molecules adsorbed on-top the Rh atoms at the steps

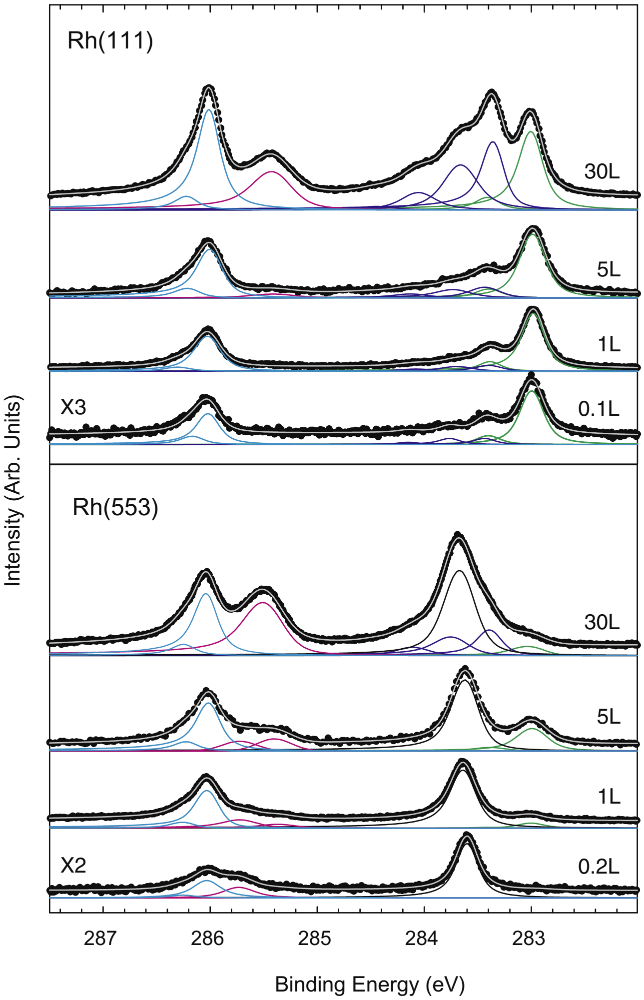

Fig. 1. C1s spectra after ethanol exposures at room temperature between 0.1 and 30 L on Rh(111) and Rh(553). The photon energy is 380 eV. Decompositions of the spectra into a number of components as explained in the text are shown.