The structure and reactivity of 2-butanol on Pd(1 1 1)

Feng Gao [a], Yilin Wang [a], Luke Burkholder [a], Carol Hirschmugl [b], Dilano K. Saldin [b], Hin Cheuk Poon [b], David Sholl [c], Joanna James [d], Wilfred T. Tysoe [a,*]

[a] Department of Chemistry and Biochemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA
[b] Department of Physics and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53211, USA
[c] School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, USA
[d] Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, PA 12345, USA

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ABSTRACT

The structure, formation and decomposition pathways of 2-butoxide species formed on a Pd(1 1 1) surface following the adsorption of 2-butanol is studied by a combination of density functional theory (DFT), analysis of the low-energy electron intensity versus beam energy curves (LEED I/E) and temperature-programmed desorption (TPD). Both DFT calculations and LEED I/E measurements reveal that 2-butoxide adsorbs with the oxygen atom located in the three-fold hollow sites on Pd(1 1 1) with the C–O bond almost perpendicular to the surface with the 2-butyl group in the trans configuration. At coverages below ~0.11 monolayers, adsorbed 2-butoxide species completely thermally decompose to desorb hydrogen and carbon monoxide. The 2-butoxide species present at higher coverages either hydrogenate to reform 2-butanol or undergo a β-hydride elimination reaction to form 2-butanone.

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1. Introduction

Pd(1 1 1) surfaces modified by adsorbed chiral 2-butanol have been shown to lead to the enantioselective chemisorption of propylene oxide. That is, pre-covering a Pd(1 1 1) surface with either *R*- or *S*-2-butanol leads to a preferential adsorption of propylene oxide of the same chirality over a narrow 2-butanol coverage range [1,2]. This effect was initially ascribed to enantioselectivity induced by chiral 2-butoxide species formed by dehydrogenation of 2-butanol [1]. However, it was found more recently that this effect was in fact due to enantiospecific hydrogen-bonding interactions between 2-butanol and propylene oxide [2]. Measurements of the variation in enantiospecificity with 2-butanol exposure suggested that propylene oxide can interact either with a single adsorbed 2-butanol molecule or, at higher coverages, with two adsorbed 2-butanol species to form enantioselective sites [3]. More recently, 2-butanol has been used as a chiral probe for enantioselectivity on surfaces modified by an amino acid [4].

Although the formation of 2-butoxide is not directly relevant to enantioselective chemisorption described above, it is nevertheless important to understand surface chemistry of 2-butanol (and other C_4+ alcohols), which have received much less attention in the past

than smaller alcohols [5,6]. Reflection–absorption infrared spectroscopy (RAIRS) revealed that the adsorbed 2-butanol dehydrogenated to form 2-butoxide, which underwent a β-hydride elimination reaction to yield 2-butanone [1]. The work described below focuses on the surface chemistry of 2-butanol in greater detail using temperature-programmed desorption (TPD) and by determining the structure of the 2-butoxide intermediate using low-energy electron diffraction (LEED) measurements. Compared with X-ray diffraction structure measurements, which may be modeled by single-scattering theory, "direct methods" for electron diffraction, a strong multiple-scattering problem, are still very much under development [7]. It is thus customary in determining surface structures using LEED to calculate experimental intensity *versus* beam energy (I/E) curves for all likely adsorbate structures and compare these with the experimental data to establish the correct structure [8]. While this approach is feasible for adsorbates with a relatively small number of degrees of freedom, it rapidly becomes prohibitive for larger molecules such as 2-butanol. In order to address this problem, the 2-butoxide structure on a Pd(1 1 1) surface is calculated using density functional theory (DFT). This provided a limited number of structures, which can then be compared with the experimental I/E curves to provide the correct surface structure.

2. Experimental methods

Temperature-programmed desorption (TPD) data were collected in an ultrahigh vacuum chamber that has been described

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* Corresponding author. Tel.: +1 414 229 5222; fax: +1 414 229 5036.
E-mail address: wtt@uwm.edu (W.T. Tysoe).

in detail elsewhere [9] where desorbing species were detected using a Dycor quadrupole mass spectrometer placed in line of sight of the sample. The temperature ramp and data collection were controlled using LabView software. All TPD spectra were recorded using a heating rate of 6.5 K/s in this study.

LEED I/E curves were measured in a low current system with an incident beam current of ∼500 fA using a system described previously [10]. The diffracted beam was amplified using a microchannel plate and the position of the amplified electron pulse determined using a wire grid system. This allowed a full I/E curve to be obtained for less than one electron interacting with each adsorbate molecule.

The Pd(111) sample was cleaned using a standard procedure which consisted of heating at 1000 K in ∼4 × 10^{-8} Torr of oxygen and then annealing at 1200 K *in vacuo* to remove any remaining oxygen. Since a strong palladium peak effectively obscures the carbon KLL Auger feature, Auger spectroscopy is insensitive to the presence of small amounts of surface carbon. A sensitive gauge of carbon coverage was to saturate the surface with oxygen and to perform a temperature-programmed desorption experiment. The presence of surface carbon is manifest by the desorption of CO. As the surface becomes depleted of carbon, the CO yield decreases and the yield of oxygen increases correspondingly. The complete absence of carbon is indicated by the desorption of only O_2.

2-butanol (Aldrich, 99.5%) was transferred to glass bottles and attached to the gas-handling systems of the vacuum chambers and was further purified by several freeze-pump-thaw cycles. The cleanliness of all reactants was monitored mass spectroscopically.

3. Theoretical methods

The I/E curves from the 2-butoxide-covered sample were simulated for normal incidence by assuming an ordered overlayer of the smallest possible (1 × 1) periodicity with fractional occupancy of the same magnitude as the coverage Θ. This idea that the intensities of integer-order beams may be calculated by considering their interactions with just other integer-order beams may be regarded as a special case of the beam set neglect method [11,12]. The additional simplification is that the quasidynamical [13] treatment of the adlayer allows it to be treated as literally a (1 × 1) overlayer with an adsorbate scattering factor reduced by a factor of Θ, so that the coverage appears as a variable in the LEED structure determination [14–18].

Plane wave density functional theory calculations were performed using the Vienna *ab initio* Simulation Package (VASP) and the ultrasoft pseudopotentials available in this package [19]. VASP has been shown to give results that are in agreement with other DFT packages [20,21]. The results reported here are from calculations with the generalized gradient approximation (GGA) using the Perdew–Wang 91 functional [22]. We used a 3 × 3 × 1 Monkhorst–Pack [23] k-point sampling of the Brillouin zone and a plane wave expansion with a cutoff of 396 eV. To examine the structure of isolated 2-butoxide on Pd(111), all calculations placed a single adsorbed molecule in a (3 × 3) surface unit cell. The Pd (111) surface was represented by a slab four layers thick with a vacuum spacing of 14 Å. The top two layers of the slab were allowed to relax with the adsorbed molecule, since the adsorbate is expected to exhibit some effect on the substrate. The DFT-optimized lattice constant for Pd was used to define the surface. This lattice constant, 3.96 Å, is in good agreement with the experimental value of 3.89 Å [24]. All calculations involved convergence of relaxed atomic forces to within 0.03 eV/Å and include dipole corrections [22,25] in the direction normal to the surface.

4. Results

4.1. Surface Structure Determination

We have shown previously that the structure of disordered overlayers can be determined from the change in the I/E curves of the substrate (1 × 1) Bragg spots due to the presence of the overlayer [14–18]. In this case, the overlayer structure is determined by simulating an ordered overlayer of the smallest possible (1 × 1) periodicity with fractional occupancy of the same magnitude as the coverage Θ. This approach has been successful in establishing the structures of a number of surface species. Comparison of the structures measured by LEED with those calculated by DFT yielded excellent agreement in all cases. Since it is a prohibitively large task to compare the calculated structures of all possible configurations of relatively large adsorbates such as 2-butoxide species, our approach is to compare the structure of 2-butoxide calculated using DFT with the experimental LEED I/E curves to establish whether the calculated structure is indeed correct.

To examine the structure of isolated 2-butoxide on Pd(111), we initially placed a single adsorbed molecule in a (3 × 3) surface unit cell with the O–C bond centered over fcc, hcp, atop and bridge sites. DFT calculations showed that the 2-butoxide adsorbs on the surface with the oxygen atom located above the Pd(111) three-fold hollow site with the O–C bond oriented approximately perpendicular to the surface. Other stable sites included those near the hcp, atop and bridge sites, but were less stable by 0.19 eV to 0.36 eV. To ensure that these molecules were isolated and that there were no interactive effects in this study, we also placed a single adsorbed molecule in a (4 × 3) surface unit cell with the butyl group oriented along the length of the unit cell. These calculations showed an identical bonding preference. The 2-butyl group is in the trans configuration with its plane oriented approximately parallel to the surface. This surface structure is shown graphically in Fig. 1 for a surface coverage of 1/9 (Θ = 0.11) and the interatomic distances and angles are given in Table 1. We also examined the azimuthal rotational energy barrier using DFT by rotating the molecule by 10° increments through 120°. Our calculations indicate that the energy barrier to azimuthal rotation is only 0.05 eV,

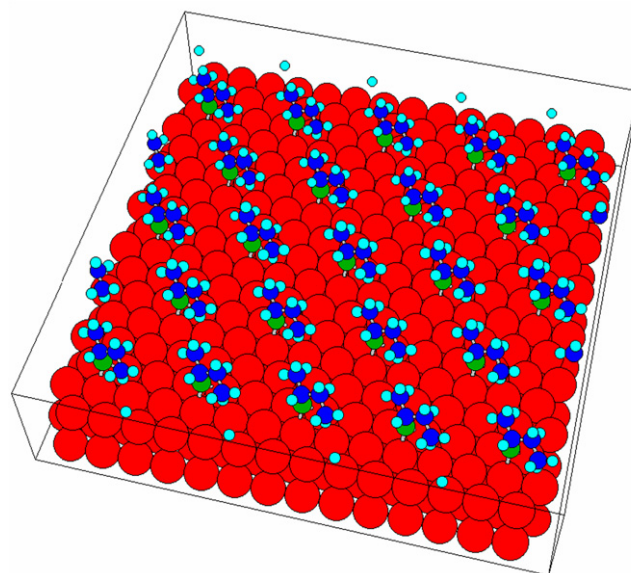Fig. 1. Schematic depiction of the structure of 2-butoxide species on a Pd(111) surface with a coverage of 0.11.