



Ethanol and ethylene glycol on Ni/Pt(1 1 1) bimetallic surfaces: A DFT and HREELS study

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ABSTRACT

The reactions of ethanol and ethylene glycol have been studied on Ni/Pt(1 1 1) bimetallic surfaces using density functional theory (DFT) and high resolution electron energy loss spectroscopy (HREELS). A linear correlation has been observed between the binding energies of ethanol, ethoxy, and ethylene glycol species and the surface *d*-band center, with increasing binding energy as the *d*-band center shifts closer to the Fermi level. HREELS measurements have identified the bond scission sequence of ethanol and ethylene glycol on Ni/Pt(1 1 1) bimetallic surfaces. Two bimetallic surfaces can be formed that possess very different chemical properties: one with a monolayer of Ni atoms on top of Pt(1 1 1) designated Ni–Pt–Pt(1 1 1), and the other with the Ni atoms diffusing into the subsurface region, designated Pt–Ni–Pt(1 1 1). At 120 K ethanol adsorbs molecularly with the O–H bond intact on Pt(1 1 1) and Pt–Ni–Pt(1 1 1), while dissociative adsorption is observed on Ni–Pt–Pt(1 1 1) and Ni(1 1 1) film surfaces. Ethylene glycol adsorbs molecularly with the O–H bond intact on all four surfaces at 200 K, and desorbs reversibly from Pt(1 1 1) and Pt–Ni–Pt(1 1 1). In contrast, ethylene glycol undergoes decomposition on Ni–Pt–Pt(1 1 1) and Ni(1 1 1) film surfaces through O–H bond cleavage, forming an ethylenedioxy (–OCH₂–CH₂O–) intermediate. This intermediate reacts by further dehydrogenation and C–C bond scission to eventually form CO. Overall, the HREELS results are consistent with TPD studies that show the reforming activities of ethanol and ethylene glycol follow the trend Ni–Pt–Pt(1 1 1) > Ni(1 1 1) film > Pt(1 1 1) > Pt–Ni–Pt(1 1 1).

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1. Introduction

The reactions of oxygenates on transition metal surfaces are important for a variety of industrial processes. The production of hydrogen from oxygenated compounds has been a topic of increasing interest as a way to alleviate the environmental impact of fossil fuel consumption. Ethanol has attracted particular interest because it can be produced from biomass, and the distillation of ethanol from fermentation of corn is already practiced industrially. Along with ethanol, ethylene glycol has been studied as a potential feedstock for hydrogen production and as a model compound for larger polyols that can be derived from biomass such as glycerol, sorbitol, glucose, etc. More detailed discussion on the reforming of oxygenates can be founded in recent reviews [1,2].

We have performed a series of surface science and DFT studies to investigate the reforming pathways of oxygenates on bimetallic surfaces [3–5]. For example, in a previous paper, we reported the reactions of ethanol and ethylene glycol on Ni/Pt(1 1 1) bimetallic surfaces using temperature programmed desorption (TPD). The Ni–Pt–Pt(1 1 1) bimetallic surface, with a monolayer Ni atoms

residing on the Pt(1 1 1) surface, exhibited increased activity for reforming of ethanol and ethylene glycol as compared to either Ni(1 1 1) or Pt(1 1 1) surfaces. The experimental reforming yield of both oxygenates [3], as well as that of glycerol [4] and methanol [5], displayed a nearly linear correlation with the surface *d*-band center as calculated by DFT, with increasing reforming activity as the *d*-band center moved closer to the Fermi level. It was predicted that other 3*d*–Pt–Pt(1 1 1) bimetallic surfaces might also be potential catalysts for reforming of oxygenates. Recent studies using supported catalysts showed that NiPt, CoPt, and FePt displayed increased turnover frequencies for aqueous phase reforming of ethylene glycol compared to Pt [6]. The focus of the current paper is on the mechanistic details of the decomposition sequence of ethanol and ethylene glycol on Ni/Pt(1 1 1) bimetallic surfaces.

The reaction of ethanol has been studied previously on a variety of transition metal surfaces, including Pt(1 1 1) [3,7–10], Ni(1 1 1) [11,12], Pd(1 1 1) [13–15], Pd(1 1 0) [15], and Rh(1 1 1) [16]. Ethanol reacts on Pt(1 1 1) to produce mainly H₂ and CO, while on Ni(1 1 1) [11] the evolution of acetaldehyde is also observed. The reaction is believed to proceed through initial O–H bond scission, forming an ethoxy species. This species can further dehydrogenate on Pt and Ni surfaces to an acetaldehyde intermediate, which decomposes to produce CO and H₂.

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Ethylene glycol has been investigated previously on Pt(111) [3], Rh(111) [17], Ni(100) [18], Cu(110) [19], Ag(110) [20,21] and Mo(110) [22]. Ethylene glycol adsorbs reversibly on clean Ag(110) [20], while on most other surfaces the decomposition has been observed to proceed by initial O–H bond cleavage, forming an ethylenedioxy intermediate ($-\text{OCH}_2\text{CH}_2\text{O}-$). This intermediate can also be formed by reaction of ethylene glycol with pre-dosed oxygen atoms on Ag(110) [20,21] and dehydrogenates on this surface to produce glyoxal (CHO)₂, as well as reacting through C–C bond scission to yield formaldehyde (H_2CO) and surface formate (HCOO). The formate species further decomposes to H_2 and CO_2 . On Pt(111) [3] and Rh(111) [17] the main products are CO and H_2 , while on Ni(100) [18] decomposition to atomic carbon and oxygen is reported to be the main reaction pathway. On Mo(110) [22] ethylene glycol adsorbs to form monodentate ($-\text{OCH}_2\text{CH}_2\text{OH}$) and bidentate ($-\text{OCH}_2\text{CH}_2\text{O}-$) species, which react primarily through C–O bond cleavage to yield ethylene, H_2 , and atomic oxygen.

In this work, we first present the results of DFT calculations of the bonding of ethanol, ethoxy and species derived from ethylene glycol on Ni–Pt–Pt(111), Pt–Ni–Pt(111), Pt(111) and Ni(111) surfaces. DFT calculations predict increased binding energies on Ni–Pt–Pt(111) as compared to Pt–Ni–Pt(111) and clean Pt(111), with the observed trend consistent with previous results for other molecules [23]. This is followed by HREELS studies of the adsorption and decomposition of ethanol and ethylene glycol on these surfaces. Ethanol adsorbs molecularly at 120 K with the O–H bond intact on Pt(111) and Pt–Ni–Pt(111), while dissociative adsorption is observed on Ni–Pt–Pt(111) and Ni(111) film to form ethoxy species, which dehydrogenate further to adsorbed CO . Ethylene glycol adsorbs molecularly on all four surfaces at 200 K. Ethylene glycol undergoes primarily reversible desorption from the Pt(111) and Pt–Ni–Pt(111) surfaces. In contrast, on Ni–Pt–Pt(111) and Ni(111) film the initial decomposition proceeds through O–H bond cleavage, forming a ($-\text{OCH}_2\text{CH}_2\text{O}-$) intermediate. This intermediate reacts through further dehydrogenation and C–C bond scission to eventually form CO on the surface.

2. Theoretical and experimental methods

2.1. DFT–VASP parameters

Theoretical calculations were performed with the VASP package [24–26], which uses a planewave basis set with pseudopotentials to represent core electrons. The PW91 functional was used for self-consistent electronic structure calculations. Each surface was approximated by a 3×3 unit cell with four layers of metal separated by six equivalent layers of vacuum, repeated periodically. The top two layers along with the adsorbates were allowed to relax to the lowest energy configuration. A planewave cutoff of 396 eV was used for all calculations. The d -band density of states was determined by projection of the planewaves onto spherical harmonic orbitals. The surface d -band center values were previously calculated [27] as the first moment of the projected d -band density of states on the surface atoms relative to the Fermi level. The binding energies of ethanol, ethoxy and species derived from ethylene glycol were determined as the difference between the energy of the slab with the adsorbate minus the energy of the slab alone and the adsorbate alone. The dissociating hydrogen atom was not included in the binding energy of the alkoxy species. The Ni(111) film surface was approximated by Ni(111) in all DFT calculations.

2.2. Techniques

The UHV chamber used for the HREELS experiments has been described previously [28,29]. It is a three-level stainless steel

chamber (base pressure 3×10^{-10} Torr) equipped with AES and TPD in the top two levels and HREELS in the bottom level. The HREELS spectra reported here were acquired with a primary beam energy of 6 eV. Angles of incidence and reflection were 60° with respect to the surface normal. Count rates in the elastic peak were typically between 2×10^4 and 5×10^4 counts per second, and the spectral resolution was between 30 and 50 cm^{-1} full width at half maximum (FWHM). Each HREEL spectrum was normalized to unity using the elastic peak intensity and then scaled by a multiplication factor as shown in the figures.

The Pt(111) single crystal (Princeton Scientific, 99.99%) was 1 mm thick, with a 10 mm diameter, and was oriented to within 0.5° . The crystal was spot welded directly to two tantalum posts that served as electronic contacts for resistive heating, as well as thermal contacts for cooling with liquid nitrogen. The sample temperature was measured by spot welding a chromel–alumel thermocouple to the top edge of the Pt(111) single crystal and could be varied between 100 and 1100 K. The Pt(111) surface was cleaned by repeated cycles of Ne^+ sputtering at 600 K and annealing at 1100 K. Following the last sputter cycle, 1 L of O_2 at 890 K was used to remove carbon left on the surface, followed by annealing at 1100 K for 5 min. This cleaning procedure was repeated until negligible C or O was detected by AES.

Ni/Pt(111) bimetallic surfaces were prepared by evaporative deposition of Ni onto Pt(111), as described earlier [30]. The crystal was held at either 600 or 300 K during deposition, depending on which bimetallic surface was being prepared. The metal doser consisted of a tungsten filament with a high purity Ni wire (Alfa Aesar, 99.99+%) wrapped around it, mounted within a tantalum enclosure. The Ni(849 eV)/Pt(241 eV) AES ratios were used to determine Ni coverages, with a ratio of 1.0 corresponding to a monolayer surface Pt–Ni–Pt(111) structure [31]. The monolayer Ni–Pt–Pt(111) surface was formed by depositing Ni onto Pt(111) at 300 K for the same deposition time as for Pt–Ni–Pt(111). For the Ni(111) film, deposition was carried out at 600 K until more than 6 ML of Ni were deposited. As reported previously, using the recombinative desorption of D_2 as a chemical probe, the as-prepared Ni(111) film produced a nearly identical TPD spectrum to that from bulk Ni(111) [32].

Ethanol (Sigma–Aldrich, 99.5+%) and ethylene glycol (Sigma–Aldrich, 99.8%) were transferred into glass sample cylinders and purified using repeated freeze–pump–thaw cycles. All other gases were of research purity and were used without further purification. The purity of all reagents was verified in situ using mass spectrometry prior to use. Doses are reported in Langmuirs ($1 \text{ L} = 1 \times 10^{-6}$ Torr s) and are uncorrected for ion gauge sensitivity.

3. Results

3.1. DFT calculations

The binding energies of ethanol, ethoxy, ethylene glycol, $-\text{OCH}_2\text{CH}_2\text{OH}$, and $-\text{OCH}_2\text{CH}_2\text{O}-$ species were calculated on Pt(111), Pt–Ni–Pt(111), Ni–Pt–Pt(111) and Ni(111) film surfaces, as shown in Fig. 1. Ethanol and ethoxy were adsorbed on an atop site through the oxygen atom as shown in Fig. 2. On Ni–Pt–Pt(111), the ethanol Ni–O bond distance and Ni–O–C bond angle were 2.02 Å and 57.8° with respect to the surface normal, respectively. After removal of the first hydrogen to produce ethoxy, the Ni–O bond distance and the Ni–O–C bond angle decreased slightly to 1.80 Å and 54.2° . The binding energies of ethanol and ethoxy on Pt(111) were found to be -6.5 and -35.4 kcal/mol, respectively, in good agreement with values of -6.5 and -32.5 kcal/mol reported in previous studies [33]. Among the four surfaces, ethanol and ethoxy species were bound

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