# Reforming of Oxygenates for H<sub>2</sub> Production: Correlating Reactivity of Ethylene Glycol and Ethanol on Pt(111) and Ni/Pt(111) with Surface d-Band Center

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The dehydrogenation and decarbonylation of ethylene glycol and ethanol were studied using temperature programmed desorption (TPD) on Pt(111) and Ni/Pt(111) bimetallic surfaces, as probe reactions for the reforming of oxygenates for the production of H<sub>2</sub> for fuel cells. Ethylene glycol reacted via dehydrogenation to form CO and H<sub>2</sub>, corresponding to the desired reforming reaction, and via total decomposition to produce  $C_{(ad)}$ ,  $O_{(ad)}$ , and H<sub>2</sub>. Ethanol reacted by three reaction pathways, dehydrogenation, decarbonylation, and total decomposition, producing CO, H<sub>2</sub>, CH<sub>4</sub>,  $C_{(ad)}$ , and  $O_{(ad)}$ . Surfaces prepared by deposition of a monolayer of Ni on Pt(111) at 300 K, designated Ni–Pt–Pt(111), displayed increased reforming activity compared to Pt(111), subsurface monolayer Pt–Ni–Pt(111), and thick Ni/Pt(111). Reforming activity was correlated with the d-band center of the surfaces and displayed a linear trend for both ethylene glycol and ethanol, with activity increasing as the surface d-band center moved closer to the Fermi level. This trend was opposite to that previously observed for hydrogenation reactions, where increased activity occurred on subsurface monolayers as the d-band center of bimetallic systems may provide useful predictions for the selection and rational design of bimetallic catalysts for the reforming of oxygenates.

## I. Introduction

Production of hydrogen for use in fuel cells can be achieved by selective reforming of oxygenates. The oxygenates may be derived from renewable biomass and offer advantages such as low toxicity, low reactivity, and compatibility with the current infrastructure for transportation and storage. Recently, aqueous phase reforming of oxygenates, such as ethylene glycol, has been studied on various transition metals.<sup>1-11</sup> The rate of reforming decreased as follows: Pt, Ni > Ru > Rh, Pd > Ir, while hydrogen selectivity showed the following trend: Pd > $Pt > Ni > Ru > Rh.^3$  Overall, Pt was identified as the most promising catalyst. Nickel-based catalysts were found to be active for reforming of ethylene glycol but also displayed decreased hydrogen selectivity due to alkane production.<sup>3</sup> Other studies have investigated the replacement of precious metal catalysts with less expensive substitutes, and a Sn/Ni bimetallic catalyst has been reported with hydrogen selectivity comparable to Pt/Al<sub>2</sub>O<sub>3</sub>.<sup>4,8-10</sup> The reforming of other oxygenates, such as ethanol, has been studied on bimetallic catalysts such as Rh-Pt,12 Au-Rh,13 and Ni-Rh.14

Bimetallic catalysts offer one approach to altering the physical and chemical properties of metals, in some cases producing unique catalytic properties not seen for either of the parent metals.<sup>15–19</sup> Recent work has demonstrated that combined experimental and theoretical studies can be used to understand the reactivity of bimetallic alloys and to predict properties of new combinations.<sup>20–32</sup>

The Ni/Pt bimetallic system displays novel catalytic properties and has been studied extensively.<sup>22–27</sup> The surface morphology of a Ni/Pt(111) bimetallic surface depends on the deposition temperature and time. Deposition of monolayer coverage Ni on Pt(111) at a substrate temperature of 600 K produces a surface with nickel atoms diffusing into the subsurface region, leaving the top layer enriched with platinum, as confirmed by STM, LEIS, XPS, and AES.<sup>23</sup> The subsurface monolayer alloy, designated as Pt-Ni-Pt(111), can be prepared by depositing either Ni onto  $Pt(111)^{25}$  or Pt onto Ni(111)<sup>24</sup> at 600 K at a monolayer Ni or Pt coverage. Longer deposition times of Ni onto Pt(111) at 600 K produce surfaces composed of several nickel layers, which begin to approximate the structure and reactivity of the Ni(111) surface. On the other hand, the deposition of monolayer Ni at 300 K leads to the Ni atoms residing on the surface, and this surface is designated as Ni-Pt-Pt(111). Annealing the surface monolayer Ni-Pt-Pt(111) prepared at 300 K to 600 K causes the Ni atoms to diffuse into the subsurface and produces a Pt-Ni-Pt(111) subsurface monolayer with similar structure and reactivity as those deposited at 600 K.<sup>23</sup>

The Ni/Pt(111) bimetallic surfaces display chemical properties different from those of either Pt(111) or Ni(111). For example, on Pt-Ni-Pt(111), the desorption temperature of hydrogen decreases significantly as compared to either Pt(111) or Ni-(111).<sup>22</sup> Since the dissociative adsorption of hydrogen is nonactivated, this suggests a weaker metal-H bond on the subsurface monolayer Pt-Ni-Pt(111). The availability of more weakly bonded hydrogen increases the activity for lowtemperature hydrogenation of molecules such as cyclohexene,<sup>22,24,27</sup> 1-hexene, and 1-butene.<sup>28</sup> Other temperature programmed desorption (TPD) experiments have shown that the decomposition of ethylene on Pt-Ni-Pt(111) is decreased compared to Pt(111) or Ni(111).<sup>22,26</sup> On the basis of HREEL spectra, this difference has been attributed to the formation of a weakly  $\pi$ -bonded intermediate on the bimetallic surface vs a

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more strongly di- $\sigma$ -bonded intermediate on the parent metals.<sup>22,26</sup> In contrast, surface monolayer Ni–Pt–Pt(111) displays very different properties. The desorption temperature of H<sub>2</sub> from Ni– Pt–Pt(111) increases significantly compared to that from Pt-(111) and is slightly higher than that from Ni(111).<sup>23</sup> This indicates a stronger metal–H bond on Ni–Pt–Pt(111) compared to either of the parent metals.

Theoretical calculations confirm these experimental observations. The hydrogen binding energy on Pt-Ni-Pt(111) calculated by DFT is lower than that on Pt(111) or Ni(111).<sup>23</sup> On the other hand, on Ni-Pt-Pt(111), the hydrogen binding energy calculated by DFT is higher than that on either of the parent metals. The origin of this effect was attributed to the change in the d-band of the bimetallic surfaces, as characterized by the surface d-band center. For Pt-Ni-Pt(111), the d-band center decreases compared to Pt(111) or Ni(111), shifting away from the Fermi level, resulting in weaker interactions with adsorbates. On the other hand, on Ni-Pt-Pt(111), the d-band center moves closer to the Fermi level thereby increasing interactions with adsorbates. A nearly linear correlation between the hydrogen binding energy and the d-band center was established for a wide range of bimetallic surfaces,<sup>29-31</sup> consistent with the theory of chemisorption by Hammer and Nørskov.32

In the current work, we investigate reactivity trends for the reforming of oxygenates, such as ethylene glycol and ethanol, on Pt(111) and Ni/Pt(111) bimetallic surfaces. The reactions of ethylene glycol have been studied previously on Cu(110),<sup>33</sup> Ni-(100),<sup>34</sup> Ag(110),<sup>35,36</sup> Rh(111),<sup>37</sup> and Mo(110),<sup>38</sup> but to our knowledge, surface science studies on Pt(111) or Ni/Pt(111) have not been performed. Ethanol has been studied previously on many surfaces, including Pt(111)<sup>39–41</sup> and Ni(111),<sup>42,43</sup> but not on Ni/Pt(111) bimetallic surfaces. TPD results for ethylene glycol and ethanol on Pt(111) and Ni/Pt(111) will be presented first, followed by correlations of the activities with the d-band center of the surfaces and predictions based on the surface d-band center of other Pt-3d metal bimetallic surfaces.

## **II. Experimental and Theoretical Methods**

2.1. Techniques. The ultrahigh vacuum (UHV) chamber used for the experiments was a two-level stainless steel chamber (base pressure of  $1 \times 10^{-10}$  Torr), which was equipped with Auger electron spectroscopy (AES) and TPD. In TPD experiments, the samples were heated at a linear rate of 3 K/s. The opening of the random flux shield of the quadrupole mass spectrometer (UTI 100C) was placed at a distance of  $\sim$ 5 mm from the sample surface. The TPD experimental setup allowed up to 12 masses to be monitored simultaneously. 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 electrical connections for resistive heating, as well as thermal contacts for cooling with liquid nitrogen. With this mounting scheme, the temperature of the crystal could be varied between 100 and 1100 K. The sample temperature was measured by spot welding a chromel-alumel thermocouple to the top edge of the Pt(111)single crystal.

Ethylene glycol (Sigma-Aldrich, 99.8%) and ethanol (Sigma-Aldrich, 99.5+%) 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 by mass spectrometry prior to use. Doses are reported in langmuirs ( $1 L = 1 \times 10^{-6}$  Torr s) and are uncorrected for ion gauge sensitivity or flux enhancement due to dosing with the

directional tubing. In all experiments, the gas exposures were made at a crystal temperature of 200 K through a 1/4 in. stainless steel tube. For ethylene glycol experiments, dosing was performed with the crystal several inches away facing the dosing tube. Ethanol experiments were performed with the crystal facing away from the dosing tube.

The Pt(111) surface was cleaned by repeated cycles of Ne<sup>+</sup> 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 physical vapor deposition (PVD) of Ni, as described earlier.<sup>22</sup> The crystal was held at either 600 or 300 K during Ni deposition, depending on which surface was being prepared. The evaporative PVD 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, similar to procedures described earlier where a Ni/Pt AES ratio of 1.0 was taken as the monolayer coverage for Pt-Ni-Pt(111).<sup>22</sup> For Ni-Pt-Pt-(111), it is more difficult to determine the morphology of the monolayer because Ni does not grow in a layer-by-layer mode at 300 K. Therefore, for this work, Ni-Pt-Pt(111) was formed by depositing Ni onto Pt(111) at 300 K for exactly the same deposition time as for monolayer Pt-Ni-Pt(111). This procedure leads to a difference in the AES Ni/Pt ratio between the Pt-Ni-Pt(111) and Ni-Pt-Pt(111) surfaces. This is because, for Pt-Ni-Pt(111), the subsurface Ni is somewhat screened by the top layer of Pt. Thus, after monolayer deposition for Ni-Pt-Pt(111), the AES ratios were approximately 1.5, as compared to 1.0 for Pt-Ni-Pt(111). For the thick Ni/Pt(111), deposition was carried out at 600 K until more than 6 ML of Ni were deposited.

2.2. DFT Modeling. Theoretical calculations were performed with the DACAPO package, which uses a plane wave basis set with pseudopotentials to represent the core electrons. The PW91 functional was used for self-consistent electronic structure calculations, with an electronic temperature of  $k_{\rm B}T = 0.2$  eV for speeding up the convergence, extrapolated back to 0 K. The surfaces were approximated by a  $2 \times 2$  unit cell with three layers of metal separated by five equivalent layers of vacuum, repeated periodically. The top layer was relaxed to the lowest energy configuration. A plane wave cutoff of 350 eV was used for all calculations. The d-band density of states was determined by projection of the plane waves onto spherical harmonic orbitals. The d-band center was calculated as the first moment of the projected d-band density of states on the surface atoms relative to the Fermi level. The Pt-Ni-Pt(111) surface was approximated by replacing the second layer Pt atoms with Ni, while for Ni-Pt-Pt(111) the topmost layer was replaced with Ni. The d-band center of the thick Ni/Pt(111) surface was approximated as that for Ni(111). For other Pt-3d bimetallic surfaces, the topmost layer was replaced with the 3d metal of interest.

#### **III. Results**

**3.1. TPD of Ethylene Glycol.** Figure 1a displays TPD spectra of ethylene glycol from Pt(111) following different initial exposures. Ethylene glycol desorbed from Pt(111) in two peaks. The higher temperature peak at 267 K saturated by 0.2 L and was attributed to monolayer desorption. The onset of a lower temperature peak at  $\sim$ 224 K was observed at 0.2 L exposure and was attributed to multilayer desorption.



Figure 1. TPD spectra of (a) ethylene glycol, (b) H<sub>2</sub>, (c) CO, and (d) CH<sub>4</sub> following different ethylene glycol exposures on Pt(111).

Ethylene glycol reacted on Pt(111) to form  $H_2$  and CO. Parts b and c of Figure 1 display H<sub>2</sub> and CO TPD spectra, respectively, following different exposures of ethylene glycol on Pt(111). H<sub>2</sub> desorption occurred at 329 K following an ethylene glycol exposure of 0.05 L. With increasing exposures, the desorption temperature of H<sub>2</sub> shifted to slightly lower temperatures. The evolution of H<sub>2</sub> was most likely desorption limited, as the peak temperature was the same as that after exposure of H<sub>2</sub> from calibration experiments not shown here, as well as literature data.<sup>22</sup> CO desorption occurred at approximately 460 K, also in agreement with our own experiments after exposure to CO and with literature data for a desorptionlimited process on Pt(111).44,45 The TPD spectra marked 0 L show the contributions to H<sub>2</sub> and CO spectra from background adsorption. For H<sub>2</sub>, background adsorption was minimal, but background adsorption of CO was significant. Both were accounted for in quantifying H<sub>2</sub> and CO yields, as explained below. Figure 1d shows the 16 amu TPD spectra, monitored to determine whether ethylene glycol reacted to form methane. Several peaks were observed; however, none could be attributed to methane. The lower temperature peaks at 228 and 267 K

occurred at the same temperature as ethylene glycol. The higher temperature peaks at approximately 460 K occurred at the same temperature as the peaks in the 28 amu spectra and were attributed to the cracking of CO in the mass spectrometer.

Figure 2a contains TPD spectra of ethylene glycol from Ni/ Pt(111) surfaces following a saturation exposure of 0.2 L ethylene glycol. Ethylene glycol desorbed in several peaks from the subsurface monolayer Pt-Ni-Pt(111). The peak at 227 K was consistent with multilayer desorption based on desorption from Pt(111). Monolayer desorption of ethylene glycol occurred from a peak centered at 257 K, with a high-temperature shoulder. From the surface monolayer Ni-Pt-Pt(111) and the thick Ni/Pt(111) surfaces, multilayer and monolayer desorption were not well resolved, suggesting that desorption from the monolayer decreased significantly. When the bimetallic surfaces are compared to Pt(111), the desorption temperature of ethylene glycol decreased slightly and the amount of chemisorbed molecules desorbed intact decreased significantly on Ni-Pt-Pt(111) and on the thick Ni/Pt(111) surfaces.

Parts b and c of Figure 2 show TPD spectra of  $H_2$  and CO, respectively, following a saturation exposure of 0.2 L ethylene



Figure 2. TPD spectra of (a) ethylene glycol, (b) H<sub>2</sub>, (c) CO, and (d) CH<sub>4</sub> following 0.2 L ethylene glycol on Pt(111) and Ni/Pt(111) surfaces.

glycol from Ni/Pt(111) bimetallic surfaces. H<sub>2</sub> desorbed from Pt-Ni-Pt(111) as a weak, broad peak centered at approximately 300 K, a slightly lower temperature compared to Pt(111). CO desorption occurred at 401 K, about 60 K lower than that from Pt(111). The decrease in the desorption temperature of CO was consistent with a desorption-limited process, as the heat of adsorption of CO should decrease on Pt-Ni-Pt(111) due to the decrease in the d-band center, as described in more detail later. Both H<sub>2</sub> and CO peak areas were reduced compared to Pt(111). From Ni-Pt-Pt(111), H<sub>2</sub> and CO desorbed from multiple overlapping peaks. H2 desorbed at 360 and 385 K, with a smaller third peak appearing as a low-temperature shoulder at 327 K. CO desorption occurred at 429 and 456 K, with a low-temperature shoulder at 401 K. Also, a fourth, much smaller peak was observed at 512 K. The peak areas of H<sub>2</sub> and CO increased significantly on the Ni-Pt-Pt(111) surface as compared to Pt(111) or Pt-Ni-Pt(111). From thick Ni/Pt(111), H<sub>2</sub> desorption occurred in a peak centered at 327 K, with a high-temperature shoulder at 360 K. CO desorbed from two overlapping peaks at 401 and 429 K, with a slight hightemperature shoulder. Similar to Ni-Pt-Pt(111), the H<sub>2</sub> and

CO peak areas from thick Ni/Pt(111) increased as compared to Pt(111) or Pt-Ni-Pt(111). Figure 2d displays the 16 amu spectra, which show that, similar to Pt(111), methane was not formed on any of the bimetallic surfaces, as all the observed peaks could be assigned to the cracking pattern of either ethylene glycol or CO.

**3.2. TPD of Ethanol.** The reactions of ethanol exhibited both similarities and differences relative to those of ethylene glycol. Figure 3a displays TPD spectra of ethanol from Pt(111) after different exposures of ethanol. Ethanol desorption occurred at 224 K. This peak saturated at an exposure of 0.3 L and was attributed to monolayer desorption, consistent with previous studies.<sup>39</sup> A multilayer peak was not observed because the dosing was performed while holding the crystal at 200 K to prevent adsorption of water from the UHV background. Although not shown here, separate experiments were performed in which ethanol was dosed at 120 K, which showed that the ethanol multilayer desorbed at 167 K, while water desorbed at 175 K, both consistent with literature results.<sup>40,41</sup> Other than the lack of water desorption, no changes in the TPD spectra were observed for dosing at 200 K as compared to 120 K.



Figure 3. TPD spectra of (a) ethanol, (b)  $H_2$ , (c) CO, and (d) CH<sub>4</sub> following different ethanol exposures on Pt(111).

Ethanol reacted on Pt(111) to form H<sub>2</sub>, CO, and CH<sub>4</sub>. Parts b–d of Figure 3 show the H<sub>2</sub>, CO, and CH<sub>4</sub> TPD spectra, respectively, after different exposures of ethanol on Pt(111). H<sub>2</sub> desorption occurred at 355 K, independent of the initial exposure of ethanol. CO desorbed from Pt(111) at 467 K, the same temperature as CO desorption from ethylene glycol. CH<sub>4</sub> desorption occurred at a peak temperature of 339 K. Methane desorption was clearly reaction limited, as the desorption temperature of molecularly adsorbed CH<sub>4</sub> from Pt(111) has been reported to be 67 K.<sup>46</sup> The other peak at 466 K in the 16 amu spectra was assigned to CO cracking by comparison with the 28 amu spectra. In general, the results presented here were in good agreement with previous studies of ethanol on Pt(111).<sup>39–41</sup>

Figure 4a displays TPD spectra for ethanol from Ni/Pt(111) bimetallic surfaces following a saturation exposure of 0.3 L ethanol. From Pt–Ni–Pt(111) and the thick Ni/Pt(111) surfaces, ethanol desorbed at approximately 230 K, just slightly higher than from Pt(111). On the other hand, from Ni–Pt–Pt(111), no ethanol desorption was observed. Parts b–d of Figure 4 show the H<sub>2</sub>, CO, and CH<sub>4</sub> TPD spectra, respectively. The reactivity of ethanol on the Ni/Pt(111) bimetallic surfaces followed the same trend as that of ethylene glycol. On Pt–Ni–Pt(111), the

reactivity of ethanol was lower compared to Pt(111). CH<sub>4</sub> was not detected, and H2 desorbed as a weak and broad peak centered at approximately 300 K. CO desorbed at 404 K, similar to CO desorption from the decomposition of ethylene glycol on this surface and about 50 K lower than that from Pt(111). From Ni-Pt-Pt(111), H<sub>2</sub> desorbed from an intense peak at 367 K. CO desorption occurred from three states, with the most intense peak at 459 K, followed by two weaker peaks at 515 and 549 K. On this surface, a relatively intense CH<sub>4</sub> peak was also detected at 339 K, the same peak temperature as from Pt(111). From thick Ni/Pt(111), H<sub>2</sub> and CO desorbed at 363 and 425 K, respectively. A small amount of CH4 was also detected at 339 K. The peak areas for H<sub>2</sub> and CO increased significantly on Ni-Pt-Pt(111) and thick Ni/Pt(111) surfaces as compared to Pt(111) or Pt-Ni-Pt(111), similar to the behavior of ethylene glycol on these surfaces.

# **IV. Discussion**

**4.1. Quantification of TPD Peak Areas.** The saturation coverage of  $H_2$  on Pt(111) is reported in the literature to be ~0.45 ML (or 0.9 ML  $H_{(a)}$ )<sup>47</sup> based on adsorption of  $D_2$  using



Figure 4. TPD spectra of (a) ethanol, (b) H<sub>2</sub>, (c) CO, and (d) CH<sub>4</sub> following 0.3 L ethanol on Pt(111) and Ni/Pt(111) surfaces.

nuclear microanalysis. The saturation coverage for CO on Pt-(111) is reported to be 0.68 ML.<sup>48</sup> In the current work, the absolute coverages of the H<sub>2</sub> and CO products were obtained by comparing their TPD peak areas with those following the saturation exposures of H<sub>2</sub> or CO on Pt(111). The CH<sub>4</sub> yields were determined using an experimentally determined sensitivity factor relative to CO by back filling the UHV system with equal concentrations of CH<sub>4</sub> and CO based on the ionization sensitivity factors of the two gases. Product yields were then calculated from the TPD results with appropriate subtraction of the background contributions.

The reaction pathways of ethylene glycol on Pt(111), Pt-Ni-Pt(111), Ni-Pt-Pt(111), and thick Ni/Pt(111) can be summarized as follows

$$a\text{HOCH}_2\text{CH}_2\text{OH} \rightarrow 2a\text{CO} + 3a\text{H}_2$$
 (1)

$$b\text{HOCH}_2\text{CH}_2\text{OH} \rightarrow 2b\text{C}_{(ad)} + 2b\text{O}_{(ad)} + 3b\text{H}_2$$
 (2)

Reaction 1 is the desired reforming reaction, producing CO and  $H_2$ . Reaction 2 represents total decomposition, producing  $H_2$ , as well as  $C_{(ad)}$  and  $O_{(ad)}$  which remain on the surface. AES

spectra taken after TPD confirmed the presence of  $C_{(ad)}$  following ethylene glycol exposures. The reforming activity, *a*, and decomposition activity, *b*, are calculated as follows using the H<sub>2</sub> and CO yields from the TPD peak areas. CO is only produced by reforming, and the value of *a* can be calculated from the CO yield. H<sub>2</sub> is produced in both reactions, thus the value of *b* can then be determined using the H<sub>2</sub> yield and the value of *a* calculated from the CO yield.

CO yield = 
$$2a \Rightarrow a = \frac{1}{2}$$
 CO yield  
H<sub>2</sub> yield =  $3a + 3b \Rightarrow b = \frac{1}{3}$  H<sub>2</sub> yield -  $a$ 

Table 1 summarizes the calculated activities and selectivities of ethylene glycol on Pt(111), Pt-Ni-Pt(111), Ni-Pt-Pt(111), and thick Ni/Pt(111). The Ni-Pt-Pt(111) surface displays the highest reforming activity and total activity. The reforming activity of the thick Ni/Pt(111) is also significantly higher compared to Pt(111). The Pt-Ni-Pt(111) surface shows the lowest reforming and total activities. It is also interesting to

TABLE 1: Reactivity of Ethylene Glycol on Pt(111) and Ni/Pt(111) Surfaces

		activity (ML)			selectivity (%)		
surface	reforming	decomposition	total	reforming	decomposition		
Pt(111)	0.030	0.004	0.034	88	12		
Pt-Ni-Pt(111)	0.025	0	0.025	100	0		
Ni-Pt-Pt(111)	0.144	0.023	0.167	86	14		
thick Ni/Pt(111)	0.122	0.016	0.138	88	12		

TABLE 2: Reactivity of Ethanol on Pt(111) and Ni/Pt(111) Surfaces

	activity (ML)				selectivity (%)		
surface	reforming	decomposition	$CH_4$	total	reforming	decomposition	$CH_4$
Pt(111)	0.025	0	0.002	0.027	93	0	7
Pt-Ni-Pt(111)	0.015	0	0	0.015	100	0	0
Ni-Pt-Pt(111)	0.074	0.003	0.010	0.087	85	3	12
thick Ni/Pt(111)	0.070	0	0.001	0.071	99	0	1

note that ethylene glycol reacts primarily through dehydrogenation and C–C bond scission on all four surfaces. The selectivity toward total decomposition representing C–O bond scission is at most 14%. This is important for hydrogen production by reforming of oxygenates because C–O bond scission is undesirable as it can lead to other products and deposit C<sub>(ad)</sub> onto the surface, deactivating the catalyst.

The reaction pathways of ethanol on Pt(111), Pt-Ni-Pt(111), Ni-Pt-Pt(111), and thick Ni/Pt(111) can be summarized as follows

$$aCH_3CH_2OH \rightarrow aCO + 3aH_2 + aC_{(ad)}$$
 (3)

$$bCH_3CH_2OH \rightarrow bCO + bCH_4 + bH_2$$
 (4)

$$cCH_3CH_2OH \rightarrow 2cC_{(ad)} + cO_{(ad)} + 3cH_2$$
 (5)

Reaction 3 is the most desirable pathway for reforming, as it produces CO, H<sub>2</sub>, and C<sub>(ad)</sub>. The last of these can be removed from the surface as CO by steam gasification with H<sub>2</sub>O or by the Boudouard reaction with  $CO_2$  ( $C_{(ad)} + CO_2 \leftrightarrow 2$  CO). Reaction 4 is a decarbonylation reaction, producing CH<sub>4</sub> along with CO and H<sub>2</sub>, which is undesired because 2 H<sub>2</sub> molecules are "lost" as methane. Reaction 5 represents total decomposition, producing H<sub>2</sub>, as well as C<sub>(ad)</sub> and O<sub>(ad)</sub> which remain on the surface. AES spectra taken after TPD confirmed the presence of  $C_{(ad)}$  following TPD experiments. The reforming activity, *a*, decarbonylation activity, b, and total decomposition activity, c, are calculated as follows using the H<sub>2</sub>, CO and CH<sub>4</sub> yields. CH<sub>4</sub> is only produced through reaction 2, and thus b equals the CH<sub>4</sub> yield. CO is produced by reforming and decarbonylation. The value of a is calculated using the CO yield and the value of b.  $H_2$  is produced in all three reactions, and thus the value of c is determined using the  $H_2$  yield along with the values of *a* and *b*.

CO yield = 
$$a + b \Rightarrow a = \text{CO yield} - b$$
  
CH<sub>4</sub> yield =  $b \Rightarrow b = \text{CH}_4$  yield  
H<sub>2</sub> yield =  $3a + b + 3c \Rightarrow c = \frac{1}{3}$  H<sub>2</sub> yield  $-a - \frac{1}{3}b$ 

Table 2 summarizes the calculated activities and selectivities of ethanol on Pt(111), Pt-Ni-Pt(111), Ni-Pt-Pt(111), and thick Ni/Pt(111). The reactivity trend of ethanol is very similar to that of ethylene glycol. The Ni-Pt-Pt(111) surface displays the highest reforming and total activities. The reforming activity of ethanol on thick Ni/Pt(111) is increased compared to Pt-(111). On the other hand, Pt-Ni-Pt(111) shows decreased activity as compared to Pt(111).

Similar to ethylene glycol, ethanol reacts primarily through dehydrogenation and the desired C–C bond scission. C–O bond scission is minimal and probably can be attributed to defect sites on the surfaces, consistent with previous studies which report negligible C–O bond scission in reactions of ethanol on both Pt(111)<sup>39</sup> and Ni(111).<sup>43</sup> Theoretical studies of surface reactions of ethanol and its derivatives also suggest that C–C bond scission should be favored, as the activation barrier for C–O bond scission is higher than that for C–C bond scission on Pt(111).<sup>49,50</sup>

It is interesting to compare the reactivity of ethanol on thick Ni/Pt(111) with literature studies on Ni(111).<sup>43</sup> On thick Ni/ Pt(111), ethanol reacts to form primarily CO and H<sub>2</sub>, with small amounts of CH<sub>4</sub>. However, on Ni(111), acetaldehyde (CH<sub>3</sub>CHO) is also produced, in addition to  $CH_4$ , CO, and  $H_2$ . The temperatures for the products common for both surfaces are similar. Also, both surfaces show negligible C-O bond scission during TPD experiments. Overall, thick (>3 ML) Ni/Pt(111) and Ni(111) display similar but not identical properties, as the thick Ni/Pt(111) surface still retains some bimetallic character. Other studies have shown that thick bimetallic surfaces often display reactivity different from the parent metals. For example, thick (>3 ML) Pd/Mo(110) and Pt/W(110) surfaces exhibit H<sub>2</sub> desorption temperatures different from pure Pd(111) and Pt-(111),<sup>31</sup> respectively. Also, the reactivity of ethylene on thick Pt/Ni(111) surfaces is different compared to Pt(111).<sup>26</sup> Further work is needed to understand these differences.

4.2. Correlation and Prediction of Activity using the Surface d-Band Center. To establish trends for different bimetallic surfaces, the reactivity of ethylene glycol and ethanol was correlated with the electronic properties of the corresponding surfaces as characterized by their d-band centers. The d-band center provides a useful measure of the electronic properties of transition metal surfaces, as the adsorption energies of small molecules have been shown to follow a nearly linear trend as a function of the d-band center.<sup>32</sup> The reforming activity of ethylene glycol and ethanol on Pt(111) and Ni/Pt(111) can be correlated with the surface d-band center, as shown in Figure 5. The correlation displays a fairly linear relationship, with activity increasing as the d-band center moves closer to the Fermi level. The reforming activity of ethylene glycol is higher than that of ethanol, in agreement with studies on Rh(111).<sup>37,51</sup> The selectivity to reforming for ethylene glycol and ethanol is shown in Figure 6 and does not display any discernible trend as a function of the d-band center. The reforming selectivity is fairly constant within experimental error for all surfaces except Pt-Ni-Pt(111) where it is slightly higher.



**Figure 5.** Correlation of ethylene glycol and ethanol reforming activity with the d-band center on Pt(111) and Ni/Pt(111) surfaces.



Figure 6. Reforming selectivity of ethylene glycol as a function of the d-band center on Pt(111) and Ni/Pt(111) surfaces.

From the experiments carried out in this work, the Ni-Pt-Pt(111) surface with the monolayer Ni residing in the top layer shows the highest reforming activity compared to either Pt-(111), thick Ni/Pt(111), or subsurface monolayer Pt-Ni-Pt-(111) surfaces. Using the experimentally determined linear trend of activity vs the surface d-band center, one can explore the reactivity of other Pt-3d bimetallic surfaces toward reforming of ethylene glycol and ethanol. It is known that for Pt-3d metal bimetallic surfaces, substituting a 3d metal in the subsurface of Pt(111) tends to decrease the d-band center, resulting in weaker interaction with adsorbed species such as hydrogen and oxygen.<sup>29</sup> Furthermore, the d-band center of the Pt-3d-Pt(111) surfaces, as compared to Pt(111), shifts further away from the Fermi level as the 3d metal moves to the left side of the periodic table. For reactions such as hydrogenation, this is desirable as the weaker binding of hydrogen is expected to increase the hydrogenation activity.52 However, the increase in hydrogenation activity does not continue for surfaces that exhibit very weak binding of hydrogen, such as Pd/Mo(110) and Pt/W(110), where



Figure 7. Prediction of ethylene glycol reforming activity on different monolayer 3d-Pt bimetallic surfaces based on extrapolation from Ni/ Pt(111) surfaces.

 $H_2$  dissociation is likely to be activated.<sup>31,53</sup> The volcanic behavior of the hydrogenation activity is consistent with Sabatier's principle that states there must be a balance in the binding energy of adsorbed species for catalytic reactions to take place.

In the current work, we consider Pt-3d bimetallic surfaces where the 3d metals occupy the top layer. As shown in Figure 7, DFT modeling results indicate that the presence of surface monolayer 3d metals on Pt(111) shifts the surface d-band center closer to the Fermi level, therefore increasing the interactions with adsorbates. By the use of the trend between activity and d-band center established experimentally in Figure 5, Figure 7 displays an extrapolation of ethylene glycol reforming activity on different 3d-Pt-Pt(111) bimetallic surfaces. A similar predictive trend can be established for ethanol. The trend predicts increased activity on surfaces with d-band centers closer to the Fermi level, opposite of the trend observed for hydrogenation reactions. The shift in the d-band of 3d-Pt-Pt(111) surfaces increases as the 3d metal moves to the left of the periodic table. If the established linear trend continues, then alloying Ti with Pt(111) is predicted to produce a surface nearly twice as active as Ni-Pt-Pt(111), the most active surface alloy in the present study, and seven times as active as Pt(111). However, the linear trend between predicted reactivity and the d-band center might not continue and a volcanic-type behavior might be observed, as reported for the hydrogenation activity of cyclohexene.53 Further experimental studies on Fe/Pt(111) and Ti/Pt(111) are under way to investigate the reactivity of ethylene glycol and ethanol on other 3d-Pt-Pt(111) bimetallic surfaces to confirm the prediction from the current study.

**4.3. Stability of the Ni**–**Pt**–**Pt**(**111**) **Surface.** Although the Ni–Pt–Pt(111) surface shows much higher reforming activity than Pt–Ni–Pt(111), experimental studies<sup>23</sup> and DFT modeling<sup>23,29</sup> indicate that monolayer 3d atoms prefer to reside in the subsurface region under UHV or reducing conditions. However, recent experimental and DFT studies<sup>54</sup> show that the surface monolayer is more thermodynamically stable than the subsurface monolayer in the presence of oxygen. For example, in the presence of  $10^{-8}$  Torr of O<sub>2</sub>, subsurface Ni atoms start to diffuse on top of Pt(111) at 450 K, while the diffusion of Co in Pt–Co–Pt(111) occurs at temperatures as low as 350 K.<sup>54</sup> Because

oxygen-containing molecules, such as water, are present in the reforming reaction environment and the reaction is carried out at approximately 500 K, $^{1-11}$  it is possible that the more active 3d surface monolayer might be present in the 3d-Pt bimetallic catalysts under reforming conditions. More direct measurements, such as careful EXAFS (extended X-ray adsorption fine structure) studies under in situ reaction conditions, would reveal whether the diffusion of subsurface 3d metals occurs during reforming.

### V. Conclusions

The reactions of ethylene glycol and ethanol have been studied on Pt(111) and Ni/Pt(111) bimetallic surfaces, as probes of the reforming of oxygenates for the production of H<sub>2</sub> for fuel cells. The following conclusions can be drawn:

(1) The surface monolayer Ni-Pt-Pt(111) displays the highest reforming activity, compared to Pt(111), subsurface monolayer Pt-Ni-Pt(111), and thick Ni/Pt(111) surfaces. Reactions involving C-O bond scission are minimal on these surfaces.

(2) A linear correlation between reforming activities of both ethylene glycol and ethanol and the d-band center of these surfaces has been established.

(3) DFT modeling has been performed to predict the reforming activity of 3d-Pt-Pt(111) bimetallic surfaces with other 3d metals as the surface monolayer. The modeling results predict that the activity should increase as the d-band center of the bimetallic surface moves closer to the Fermi level, which can be achieved by choosing 3d metals from the left side of the periodic table. The activity trend for the reforming of oxygenates is the opposite of that observed for hydrogenation reactions on Pt-3d bimetallic surfaces.

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#### **References and Notes**

(1) Shabaker, J. W.; Davda, R. R.; Huber, G. W.; Cortright, R. D.; Dumesic, J. A. J. Catal. 2003, 215, 344.

- (2) Shabaker, J. W.; Huber, G. W.; Davda, R. R.; Cortright, R. D.; Dumesic, J. A. Catal. Lett. 2003, 88, 1.
- (3) Davda, R. R.; Shabaker, J. W.; Huber, G. W.; Cortright, R. D.; Dumesic, J. A. Appl. Catal., B 2003, 43, 13.
- (4) Shabaker, J. W.; Huber, G. W.; Dumesic, J. A. J. Catal. 2004, 222, 180.
- (5) Cortright, R. D.; Davda, R. R.; Dumesic, J. A. Nature 2002, 418, 964
- (6) Davda, R. R.; Dumesic, J. A. Chem. Commun. 2004, 1, 36.
- (7) Davda, R. R.; Dumesic, J. A. Angew. Chem., Int. Ed. 2003, 42, 4068
- (8) Huber, G. W.; Shabaker, J. W.; Dumesic, J. A. Science 2003, 300, 2075.

- (9) Shabaker, J. W.; Dumesic, J. A. Ind. Eng. Chem. Res. 2004, 43, 3105
- (10) Shabaker, J. W.; Simonetti, D. A.; Cortright, R. D.; Dumesic, J. A. J. Catal. 2005, 231, 67.
- (11) Davda, R. R.; Shabaker, J. W.; Huber, G. W.; Cortright, R. D.; Dumesic, J. A. Appl. Catal., B 2005, 56, 171.
- (12) Sheng, P. Y.; Yee, A.; Bowmaker, G. A.; Idriss, H. J. Catal. 2002, 208, 393.
- (13) Sheng, P. Y.; Idriss, H. J. Vac. Sci. Technol., A 2004, 22, 1652. (14) Kugai, J.; Velu, S.; Song, C. Catal. Lett. 2005, 101, 255.
- (15) Goodman, D. W. Ultramicroscopy 1990, 34, 1.
- (16) Berlowitz, P. J.; Houston, J. E.; White, J. M.; Goodman, D. W. Surf. Sci. 1988, 205, 1.
  - (17) Berlowitz, P. J.; Goodman, D. W. Surf. Sci. 1987, 187, 463.
  - (18) Rodriguez, J. A. Surf. Sci. Rep. 1996, 24, 223.
- (19) Sinfelt, J. H. Bimetallic Catalysts: discoveries, concepts, and applications; Wiley: New York, 1983.
  - (20) Greeley, J.; Mavrikakis, M. Nat. Mater. 2004, 3, 810.
  - (21) Hammer, B.; Nørskov, J. K. Nature 1995, 376, 238.
- (22) Frühberger, B.; Eng, J., Jr.; Chen, J. G. Catal. Lett. 1997, 45, 85. (23) Kitchin, J. R.; Khan, N. A.; Barteau, M. A.; Chen, J. G.;
- Yahskinskiy, B.; Madey, T. E. Surf. Sci. 2003, 544, 298.
- (24) Khan, N. A.; Zellner, M. B.; Chen, J. G. Surf. Sci. 2004, 556, 87. (25) Khan, N. A.; Hwu, H. H.; Chen, J. G. J. Catal. 2002, 205, 259. (26) Khan, N. A.; Zellner, M. B.; Murillo, L. E.; Chen, J. G. Catal. Lett. 2004, 95, 1.
- (27) Hwu, H. H.; Eng, J., Jr.; Chen, J. G. J. Am. Chem. Soc. 2002, 124, 702.
- (28) Murillo, L. E.; Khan, N. A.; Chen, J. G. Surf. Sci. 2005, 594, 27. (29) Kitchin, J. R.; Nørskov, J. K.; Barteau, M. A.; Chen, J. G. J. Chem. Phys. 2004, 120, 10240.
- (30) Kitchin, J. R.; Nørskov, J. K.; Barteau, M. A.; Chen, J. G. Phys. Rev. Lett. 2004, 93, 156801.
- (31) Zellner, M. B.; Goda, A. M.; Skoplyak, O.; Barteau, M. A.; Chen, J. G. Surf. Sci. 2005, 583, 281.
- (32) Hammer, B.; Nørskov, J. K. Adv. Catal. 2000, 45, 71.
- (33) Bowker, M.; Madix, R. J. Surf. Sci. 1982, 116, 549.
- (34) Madix, R. J.; Yamada, T.; Johnson, S. W. Appl. Surf. Sci. 1984, 19.43
- (35) Capote, A. J.; Madix, R. J. Surf. Sci. 1989, 214, 276.
- (36) Capote, A. J.; Madix, R. J. J. Am. Chem. Soc. 1989, 111, 3570.
   (37) Brown, N. F.; Barteau, M. A. J. Phys. Chem. 1994, 98, 12737.
- (38) Queeney, K. T.; Arumainayagam, C. R.; Weldon, M. K.; Friend,
- C. M.; Blumberg, M. Q. J. Am. Chem. Soc. 1996, 118, 3896. (39) Lee, A. F.; Gawthrope, D. E.; Hart, N. J.; Wilson, K. Surf. Sci. 2004. 548. 200.
- (40) Sexton, B. A.; Rendulic, K. D.; Hughes, A. E. Surf. Sci. 1982, 121, 181
- (41) Rendulic, K. D.; Sexton, B. A. J. Catal. 1982, 78, 126.
- (42) Xu, J.; Zhang, X.; Zenobi, R.; Yoshinobu, J.; Xu, Z.; Yates, J. T. Surf. Sci. 1991, 256, 288.
- (43) Gates, S. M.; Russell, J. N., Jr.; Yates, J. T., Jr. Surf. Sci. 1986, 171.111
- (44) Kostov, K. L.; Jakob, P.; Menzel, D. Surf. Sci. 1997, 377-379, 802.
- (45) Thomas, V. D.; Schwank, J. W.; Gland, J. L. Surf. Sci. 2000, 464, 153.
- (46) Sloan, D. J. A.; White, J. M. Surf. Sci. 1996, 365, 212.
- (47) Norton, P. R.; Davies, J. A.; Jackman, T. E. Surf. Sci. 1982, 121, 103.
- (48) Ertl, G.; Neumann, M.; Streit, K. M. Surf. Sci. 1977, 64, 393.
- (49) Gursahani, K. I.; Alcalá, R.; Cortright, R. D.; Dumesic, J. A. Appl. Catal., A 2001, 222, 369.
- (50) Alcalá, R.; Mavrikakis, M.; Dumesic, J. A. J. Catal. 2003, 218, 178
  - (51) Houtman, C. J.; Barteau, M. A. J. Catal. 1991, 130, 528.
- (52) Khan, N. A.; Murillo, L. E.; Chen, J. G. J. Phys. Chem. B 2004, 108, 15748.
  - (53) Zellner, M. B.; Chen, J. G. J. Catal. 2005, 235, 393.
  - (54) Hwu, H. H.; Menning, C. A.; Chen, J. G. Manuscript in preparation.