A comparison of similarities and differences in the activities of Pt/Ni(111) and Ni/Pt(111) surfaces

Neetha A. Khan[a], Michael B. Zellner[a], Luis E. Murillo[a], and Jingguang G. Chen[b,*]

[a]*Department of Materials Science and Engineering, Center for Catalytic Science and Technology (CCST), University of Delaware, Newark, DE 19716*

[b]*Department of Chemical Engineering, Center for Catalytic Science and Technology (CCST), University of Delaware, Newark, DE 19716*

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The decomposition of ethylene and the self-hydrogenation of cyclohexene have been used as probe reactions to compare the activities of Ni/Pt(111) and Pt/Ni(111) surfaces. Ethylene decomposes on both pure Pt(111) and Ni(111) surfaces. Both the 1 monolayer (ML) Ni/Pt(111) and 1 ML Pt/Ni(111) surfaces exhibit a decrease in activity toward ethylene decomposition as compared to either Pt(111) or Ni(111). At higher metal coverages (~3 ML), however, the Pt/Ni(111) surface remains less active, but the Ni/Pt(111) surface becomes Ni-like toward ethylene decomposition. The comparative study of cyclohexene reaction pathways further reveals the different activities between the ~3 ML Pt/Ni(111) and ~3 ML Ni/Pt(111) surfaces.

KEY WORDS: bimetallic; cyclohexene; ethylene; Ni/Pt(111); Pt/Ni(111).

1. Introduction

Bimetallic catalysts are known to have higher activity and/or selectivity for various catalytic reactions than the pure metal catalysts. For over 20 years, scientists have used model bimetallic surfaces and chemical, electronic and physical probes to understand, at an atomic level, the activity seen in these bimetallic systems. Pioneering work in surface science by Goodman and coworkers showed a strong correlation between the CO desorption temperature and the core electron energy shift in bimetallic surfaces [1–3]. They found depositing metals, such as Ni, Pd and Cu, on W(110), Ru(0001) and Mo(110) changes the desorption temperature of CO, which correlates with the negative or positive core level binding energy shift of the metal overlayer . The interaction between the two metals can also alter other chemical reactions that occur on these bimetallic surfaces.

The focus of this paper is to compare the reactivities on Ni/Pt(111) and Pt/Ni(111) bimetallic surfaces. We have previously reported detailed studies of the novel reaction pathways of cyclohexene on Ni/Pt(111) and Pt/Ni(111) surfaces (5, N.A. Khan *et al.*, submitted for publication). On surfaces with a monolayer (ML) Ni or Pt coverage, the two surfaces exhibit similar activities. At higher coverages of Ni on Pt(111), the surfaces begin to exhibit Ni-like properties. However, as the Pt coverage on Ni(111) increases, the surface does not acquire Pt-like properties. The difference in activities between these surfaces may be a result of the strain on the Pt overlayer due to the 11% lattice mismatch between Pt (Pt–Pt bond distance = 2.77 Å) and Ni (Ni–Ni bond distance = 2.49 Å) [6] . In this paper, we will use ethylene as a probe molecule to demonstrate the similarities and differences between the Ni/Pt(111) and Pt/Ni(111) surfaces. In addition, we will also use the self-hydrogenation cyclohexene to further highlight the differences in the cyclohexene reaction pathways between the Ni/Pt(111) and Pt/Ni(111) surfaces with higher metal coverages (~3 ML).

2. Experimental

Two ultrahigh-vacuum (UHV) chambers were used in the current investigation. The TPD study was preformed in a two-level stainless steel chamber (base pressure of 1×10^{-10} Torr) equipped with Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD). For the TPD experiments, the Ni(111) or Pt(111) surface was heated with a linear heating rate of 3 K/s. The opening of the random flux shield of the quadrupole mass spectrometer was placed at a distance of ~5 mm from the sample surface. The experimental setup allowed us to monitor up to 12 masses simultaneously. The high-resolution electron energy loss spectroscopy (HREELS) chamber is also a two-level stainless steel chamber (base pressure of 6×10^{-10} Torr) equipped with AES, a mass spectrometer for TPD, and an HREELS unit. This chamber is described elsewhere in detail [7]. For HREELS experiments, the surface was heated to the specified temperature with a linear heating rate of 3 K/s, held for 5 s, then cooled to 100 K to perform measurements. Typical resolution of 40–60 cm^{-1} was obtained for all scans, using a 6 eV incident electron beam.

* To whom correspondence should be addressed.
E-mail: jgchen@udel.edu

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The Pt single crystal sample was a [111] oriented, 1.5 mm thick platinum disk (99.999%), 10 mm in diameter. The Ni single crystal was a [111] oriented, 1.5 mm thick Nickel single crystal (99.999%), 8 mm in diameter. The crystals were 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 crystals could be varied between 90 and 1200 K. The crystal surfaces were cleaned with O_2 treatment and by Ne sputtering, followed by annealing at 1000 K (Ni substrate) and 1100 K (Pt substrate). Surface cleanliness was monitored using AES.

The overlayer metal was deposited from an evaporative doser, consisting of a tungsten filament with either a Ni or Pt high purity wire wrapped around it, mounted on a stainless steel enclosure. The bimetallic surfaces were prepared with the crystal temperature maintained at 600 K. The coverages and cleanliness were measured by AES. Impurities remained less than 1% on the surface (AES atomic ratios) during deposition, with the chamber pressure $< 1 \times 10^{-9}$ Torr during evaporation of each metal. The coverage of the Pt/Ni(111) overlayer was estimated using the Pt(241 eV)/Ni(102 eV) AES ratio [N.A. Khan *et al.*, submitted for publication]. The coverage of the Ni/Pt(111) overlayer was estimated using the Ni(849 eV)/Pt(241 eV) AES ratio [8].

Cyclohexene (c-C_6H_{10}), (Aldrich, 99 + % purity) was purified by successive freeze-pump-thaw cycles prior to its use. The purity was verified *in situ* by mass spectrometry. Ethylene and Neon were all of research grade purity (99.999%) and were introduced into the UHV chamber without further purification. Doses are reported in Langmuirs (1 Langmuir (L) = 1×10^{-6} Torr s) and are uncorrected for ion gauge sensitivities. Cyclohexene dosings were made with a crystal temperature of 110 K or below and by backfilling the chamber through leak valves. Ethylene was dosed through a directional dosing tube, with a diameter of ~8 mm, which allowed for a high coverage without disrupting the chamber pressure.

3. Results and discussion

3.1. Ethylene as the probe molecule

Figure 1a shows the desorption of hydrogen from the decomposition of ethylene on Ni/Pt(111) surfaces. On the clean Pt(111) surface, hydrogen desorbs from the surface in two peaks at ~289 and ~490 K, which are similar to that seen in previous studies [5,9]. However, adding Ni to the surface reduces the activity toward decomposition, as indicated by the decrease in the hydrogen desorption peak area on the Ni/Pt(111) surface with 0.5 ML Ni. The activity, as judged from the hydrogen peak area, remains low at Ni coverages of 0.5–0.9 ML. At a higher Ni coverage (~3 ML), the activity toward decomposition increases considerably, with two peaks of hydrogen desorption occurring at 315 K and 380 K. The temperature of hydrogen desorption from the ~3 ML Ni film seems to be gradually approaching the properties of the Ni(111) surface.

Figure 1b shows the ethylene decomposition activity on Pt/Ni(111) surfaces. On Ni(111), hydrogen desorbs from the surface in two overlapping broad peaks, centered at ~363 and ~405 K. Bertolini and Rousseau suggest that the hydrogen desorption comprises of two peaks that are a result of the dehydrogenation to C_2H_2 at ~363 K and the further decomposition to atomic C and H_2 at 405 K [10]. When Pt is deposited on the Ni(111) surface at a coverage of 0.4 ML Pt, the activity of the surface toward the decomposition of ethylene decreases, as judged from the decrease in the H_2 peak area. At a coverage of 1.3 ML Pt, the H_2 peak becomes broader, with the first peak shifting to a lower temperature of ~300 K. At a Pt coverage of ~3 ML, the H_2 peak area and desorption temperature remain similar to the ML Pt/Ni(111) surface. Therefore, in contrast to the Ni-like properties on the high coverage Ni/Pt(111) surfaces, higher coverages of Pt do not act similarly to the Pt(111) surface.

We have performed HREELS measurements to provide more insight into the reaction pathway of ethylene on the Ni/Pt(111) and Pt/Ni(111) surfaces. The vibrational studies of ethylene on clean Pt(111) and Ni(111) have been investigated extensively and will not be discussed here [8–10]. Our HREELS results (not shown) are in agreement with previous studies that ethylene bonds strongly (di-σ bonded) to Pt(111) or Ni(111) at 100 K, which undergoes dissociation at higher temperatures. HREEL spectra following the adsorption of ethylene on the Ni/Pt(111) and Pt/Ni(111) surfaces are compared in figure 2. On the 1.2 ML Ni/Pt(111) surface, the presence of the relatively intense $\omega_s(=CH_2)$ mode at 947 cm^{-1} and the detection of the $\nu(=CH_2)$ mode at 3003 cm^{-1} are characteristic of weakly bonded ethylene [9]. The fact that C_2H_4 is weakly bonded on this surface is in agreement with the TPD observation of smaller degree of ethylene dissociation on the ~1 ML Ni/Pt(111) surface. For comparison, the characteristic $\omega_s(=CH_2)$ and $\nu(=CH_2)$ modes are also detected on the 1 ML Pt/Ni(111) surface at 967 and 3003 cm^{-1}, respectively. This observation qualitatively agrees with the TPD results of weaker interactions of ethylene on the 1 ML Pt/Ni(111) surface. Therefore, the combined TPD (figure 1) and HREELS (figure 2) results confirm that both the 1 ML Ni/Pt(111) and 1 ML Pt/Ni(111) surfaces interact with ethylene more weakly than either Pt(111) or Ni(111).

In addition, the HREELS results reveal differences in the interaction of ethylene on Ni/Pt(111) and Pt/Ni(111) at higher metal coverages. On the > 3 ML Ni/Pt(111) surface, the vibrational spectrum is characteristic of adsorbed acetylene [7], indicating that the > 3 ML

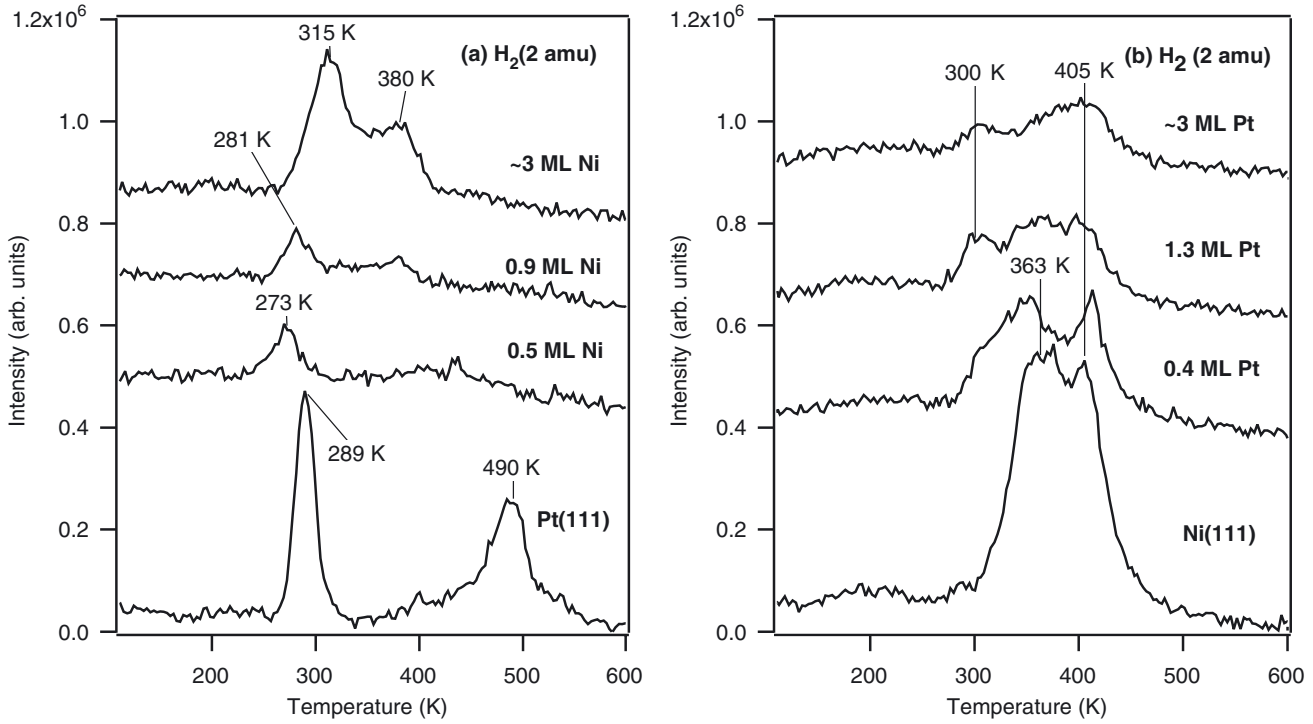

Figure 1. TPD spectra of H_2 (2 amu) desorption from the decomposition of ethylene on (a) Ni/Pt(111) surfaces and (b) Pt/Ni(111) surfaces.

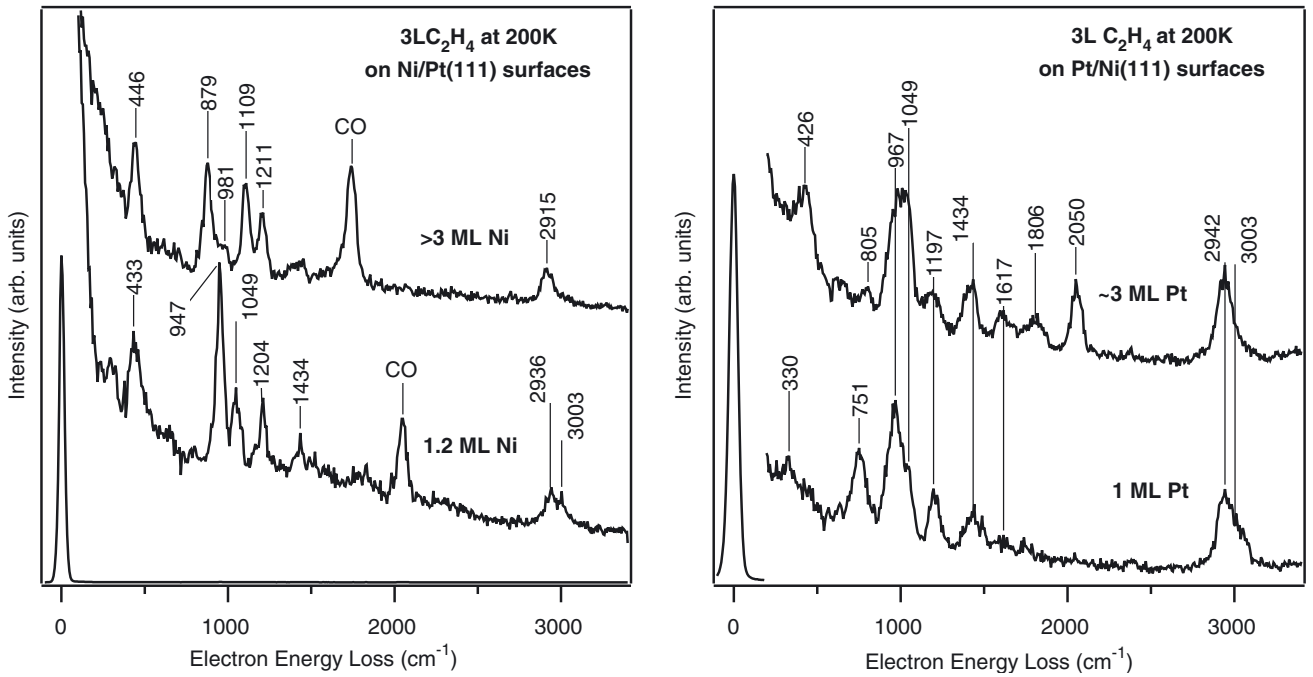

Figure 2. HREELS of 3 L ethylene exposure at 100 K, then heated to 200 K on (a) Ni/Pt(111) surfaces and (b) Pt/Ni(111) surfaces.

Ni/Pt(111) surface is active toward the dissociation of ethylene. This is in agreement with the TPD result on the ~3 ML Ni/Pt(111) surface. In contrast, the HREEL spectrum on the ~3 ML Pt/Ni(111) surface is very similar to that of the 1 ML Pt/Ni(111) surface, indicating that the ~3 ML Pt/Ni(111) surface remains less active toward the dissociation of ethylene. This observation is again in agreement with the corresponding TPD results in figure 1.

3.2. *Cyclohexene as the probe molecule*

The purpose of using cyclohexene as a probe molecule is to further confirm the different activities

of ~3 ML Ni/Pt(111) and ~3 ML Pt/Ni(111). More detailed discussion of the low-temperature hydrogenation of cyclohexene on the 1 ML Ni/Pt(111) and 1 ML Pt/Ni(111) surfaces has been published previously [5, N.A. Khan *et al.*, submitted for publication]. The three main reaction pathways of cyclohexene are self-hydrogenation, dehydrogenation, and decomposition. Shown in figure 3 is the production of cyclohexane, which is from the self-hydrogenation of cyclohexene on Ni/Pt(111) and Pt/Ni(111) surfaces. On a clean Pt(111) surface, cyclohexene does not self-hydrogenate to form cyclohexane. The presence of 0.5 ML Ni on Pt(111) leads to a small amount of cyclohexane desorbing from the surface. At ~1 ML Ni, cyclohexane is produced at 231 K. As more Ni is deposited, the activity toward hydrogenation decreases and becomes negligible at Ni coverages of ~3 ML. Similar to Pt(111), the pure Ni(111) surface does not hydrogenate cyclohexene. As 0.4 ML Pt is deposited on the Ni(111) surface, a small amount of cyclohexane begins to desorb at 237 K. At ~0.9 ML Pt, the amount of cyclohexane product increases by two-fold. In contrast to the ~3 ML Ni/Pt(111) surfaces, the ~3 ML Pt/Ni(111) surface produces cyclohexane at 237 K in a similar fashion as the 1 ML Pt/Ni(111) surface.

In order to quantify the similarities and differences, table 1 shows the comparison of activities of the Ni/Pt(111) and Pt/Ni(111) surfaces toward the self-hydrogenation and dehydrogenation reaction pathways of cyclohexene, estimated from the TPD peak areas and AES measurements. The details of the calculations have been described in previous publications [5, N.A. Khan *et al.*, submitted for publication]. However, we must note that a miscalculation was found in our earlier work in ref. [5], where the activity for the clean Pt(111) reference surface was mistakenly chosen as 0.09 c-C_6H_{10} molecules/Pt atom for dehydrogenation and 0.03 c-C_6H_{10} molecules/Pt for complete decomposition. This led to a systematic error in the product yield on the Ni/Pt(111) surfaces in ref [5]. In the current paper, we have recalculated the activity for the Ni/Pt(111) surface, using a corrected Pt(111) reference as described below using equations (1–8). Briefly, the reactions of cyclohexene on Pt(111) and 0.9 ML Ni/Pt(111) are shown below:

Table 1
Relative activity and selectivity of the Pt/Ni(111) and Ni/Pt(111) surfaces toward cyclohexene dehydrogenation and hydrogenation

Surface	Activity (molecules/metal atom)		Selectivity (c-C_6H_{12}/C_6H_6)
	C_6H_6	c-C_6H_{12}	
1 ML Ni/Pt(111)	0.031	0.002	0.07
1 ML Pt/Ni(111)	0.027	0.004	0.15
~3 ML Ni/Pt(111)	0.015	0	0
~3 ML Pt/Ni(111)	0.028	0.004	0.14

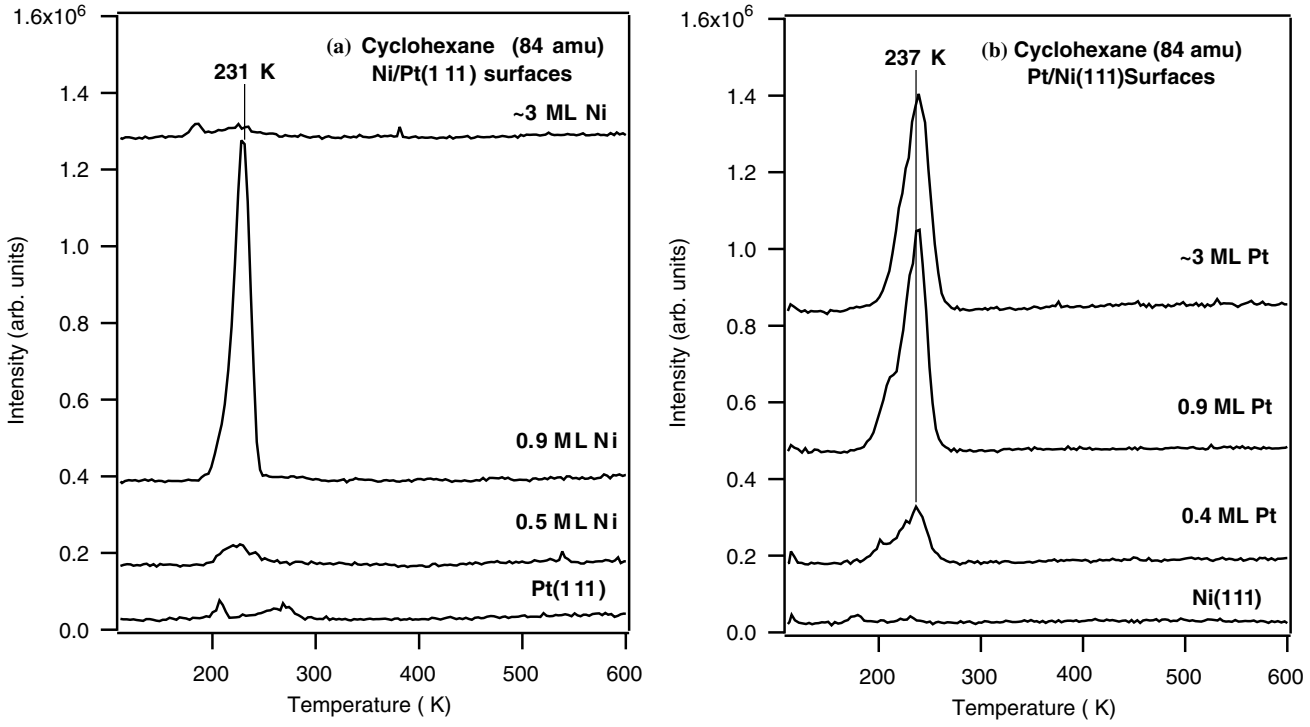

Figure 3. TPD spectra of cyclohexane (84 amu) desorption from the hydrogenation of cyclohexene on (a) Ni/Pt(111) surfaces and (b) Pt/Ni(111) surfaces.

Pt(111):

$$a\,c - C_6H_{10} \rightarrow 6a\,C_{(a)} + 5a\,H_2 \quad (1)$$

$$b\,c - C_6H_{10} \rightarrow b\,C_6H_6 + 2b\,H_2 \quad (2)$$

0.9 ML Ni/Pt(111):

$$c\,c - C_6H_{10} \rightarrow 6c\,C_{(a)} + 5c\,H_2 \quad (3)$$

$$d\,c - C_6H_{10} \rightarrow d\,C_6H_6 + 2d\,H_2 \quad (4)$$

$$e\,c - C_6H_{10} + e\,H_2 \rightarrow e\,c - C_6H_{12} \quad (5)$$

The cyclohexene activities for the Pt(111) surface were calculated in detail by Rodriguez and Campbell [11]. Using the AES ratios after a 3 L exposure and the values calculated by Rodriguez and Campbell, the activity toward decomposition and dehydrogenation was estimated to be 0.087 c-C_6H_{10} molecules/Pt atom and 0.032 c-C_6H_{10} molecules/Pt atom, respectively.

To calculate the activity toward cyclohexene dehydrogenation on the 1 ML Ni/Pt(111) surface, the peak areas of benzene desorption from a Pt(111) and 1 ML Ni/Pt(111) surface were compared, as shown in equation (6). This calculation leads to a value of 0.031 for d.

$$\frac{\text{AREA } C_6H_6 \text{ from Pt(111)}}{\text{AREA } C_6H_6 \text{ from Ni/Pt(111)}} = 1.01 = \frac{0.032}{d} \quad (6)$$

The activity for cyclohexene hydrogenation on 1 ML Ni/Pt(111) was calculated by comparing the activity of dehydrogenation to that of hydrogenation on 1 ML Ni/Pt(111), shown in equation (7). The mass spectrometer sensitivity for cyclohexane and benzene was first measured and calculated. The mass spectrometer intensity ratio was determined to be 0.41 c-C_6H_{12}/C_6H_6 by taking into consideration the different ion gauge sensitivities for c-C_6H_{12} (6.4) and C_6H_6 (5.9) and exposing the chamber to equal pressures c-C_6H_{12} (6.4×10^{-8} Torr) and C_6H_6 (5.9×10^{-8} Torr). This method led to a cyclohexane activity (e) of 0.002 c-C_6H_{10} molecules/Pt atom.

$$\frac{\text{AREA } C_6H_6 \text{ from Ni/Pt(111)}}{\text{AREA } c\text{-}C_6H_6 \text{ from Ni/Pt(111)}} * (0.41) = 16.4 = \frac{d}{e} \quad (7)$$

The calculation for the decomposition activity on the 1 ML Ni/Pt(111) surface was performed using the peak areas of hydrogen desorption. As shown in equations (1–5), the hydrogen desorption is a function of the amount of hydrogen produced in the dehydrogenation and decomposition reactions (a and b or c and d) and the hydrogen consumed in the hydrogenation reaction (e). The value for c can then be calculated to be 0.043 c-C_6H_{10} molecules/Pt atom using equation (8). The calculated activity and selectivity of the two surfaces is summarized in table 1.

$$\frac{\text{AREA } H_2 \text{ from Pt(111)}}{\text{AREA } H_2 \text{ from Ni/Pt(111)}} = 1.8 = \frac{5a + 2b}{5c + 2d - e} \quad (8)$$

As summarized in table 1, the product yield for the 1 ML Ni/Pt(111) surface was calculated to be 0.031 C_6H_6 molecules/Pt atom and 0.002 c-C_6H_{12} molecules/Pt atom. Similarly, the activity for the 1 ML Pt/Ni(111) surface was calculated to be 0.027 C_6H_6 molecules/Ni atom and 0.004 c-C_6H_{12} molecules/Ni atom. This table clearly shows that both ML surfaces have similar activities toward dehydrogenation and self-hydrogenation. The activities of the ~3 ML Ni/Pt(111) and Pt/Ni(111) surfaces are also included in table 1. The ~3 ML Pt/Ni(111) surface maintains the activity of 0.028 C_6H_6 molecules/Ni atom and 0.004 c-C_6H_{12} molecules/Ni atom, but the ~3 ML Ni/Pt(111) surface does not produce any cyclohexane and the benzene activity decreases by 50%. For ease of comparison, we also included the ratio of c-C_6H_{12}/C_6H_6 activities in the last column of the table.

3.3. Origin of similar activities on the 1 ML Ni/Pt(111) and 1 ML Pt/Ni(111) surfaces

The structures of the 1 ML Ni/Pt(111) and 1 ML Pt/Ni(111) surfaces have been analyzed in detail previously [8, 12, N.A. Khan *et al.*, submitted for publication]. Our combined scanning tunneling microscopy (STM), low-energy ion scattering spectroscopy (LEIS) and density functional theory (DFT) study revealed that Ni forms multilayers on Pt(111) at room temperature. At ~600 K, which is the temperature used in the current paper, Ni starts to diffuse into the Pt subsurface, possibly forming a subsurface Ni–Pt alloy structure [12]. The surface segregation of Pt is favored thermodynamically [13], and is consistent with previous observation of Pt enrichment on $Pt_{50}Ni_{50}$(111) single crystal alloys [14]. For deposition of Pt on Ni(111), Deckers *et al.* found that Pt grows on Ni(111) in a disordered layer-by-layer method at room temperature. Annealing this surface to higher temperatures causes a Ni–Pt surface alloy to form, with likely Pt enrichment in the surface layer and Ni enrichment in the deeper layers [6]. Therefore, the 1 ML Ni/Pt(111) and 1 ML Pt/Ni(111) surfaces should both have a Pt-enriched top layer and a Ni-enriched second layer.

As discussed in our recent DFT modeling study of Pt-based bimetallic surfaces [12,15], the presence of subsurface Ni causes a shift in the center of the d-band of Pt away from the Fermi level, which can explain the weaker interaction of ethylene on 1 ML Ni/Pt(111) and 1 ML Pt/Ni(111) [16] as compared to that on Ni(111) or Pt(111). Furthermore, the shift in the d-band center also results in a weaker metal–H bond, as verified in our recent experimental measurements of the desorption temperature of H_2 from 1 ML Ni/Pt(111) [8,12,17] and 1 ML Pt/Ni(111) [N.A. Khan *et al.*, submitted for publications]. The weaker metal–H bond should facilitate the hydrogen transfer in the self-hydrogenation of cyclohexene, as confirmed by the detection of the cyclohexane product in figure 3.

3.4. Possible origin of different activities between ~3 ML Ni/Pt(111) and ~3 ML Pt/Ni(111) and the pure Pt(111) and Ni(111) surfaces

The TPD results in figures 1 and 3 clearly indicate that the ~3 ML Pt/Ni(111) surface does not show Pt(111)-like chemical properties, but the ~3 ML Ni/Pt(111) surface exhibits Ni(111)-like chemical properties. Such a difference in activity can be explained by the different physical structures of the Ni/Pt(111) and Pt/Ni(111) surfaces at higher metal coverages. A previous study of the Ni/Pt(111) surface found that thick films of Ni on Pt(111) were characterised by a (1×1) LEED pattern, indicating a (111) film of Ni had been formed [8]. However, LEED studies on coverages of Pt on Ni(111) greater than 1 ML Pt revealed a more complex growth mechanism. Deckers *et al.* have used a combination of LEED and AES to show that Pt grows on Ni as a disordered layer [6,18].

The different growth mechanism at >1 ML coverage can be explained by the lattice mismatch between Ni (2.49 Å) and Pt (2.77 Å). It should be easier to achieve epitaxial growth of smaller atoms (Ni) on the substrate of larger atoms (Pt) than the reverse process. This can explain the formation of an epitaxial Ni film, and therefore the Ni-like properties, on Ni/Pt(111) surfaces with Ni coverages at 3 ML. On the other hand, Pt overlayers on Ni(111) should experience a strong compressive strain, which would modify the chemical properties so that a Pt film would remain less active than Pt(111) [19]. More structural characterization, such as using STM and LEIS, will be necessary to further understand the structure of the Pt/Ni(111) surfaces.

4. Conclusions

This paper discusses the similarities and differences between the Ni/Pt(111) and Pt/Ni(111) surfaces in the ethylene and cyclohexene surface chemistry. Both 1 ML Ni/Pt(111) and Pt/Ni(111) surfaces exhibit a decrease in activity toward ethylene decomposition as compared to either Pt(111) or Ni(111). At higher coverages, however, the Pt/Ni(111) surface remains less active, but the Ni/Pt(111) surface becomes more active toward ethylene decomposition. In regards to the cyclohexene chemistry on the surfaces, both ML surfaces produce the self-hydrogenation product, cyclohexane. At ~3 ML coverages, only the Pt/Ni(111) surface produces cyclohexane. This study clearly shows that the monolayer Ni/Pt(111) and Pt/Ni(111) surfaces exhibit similar chemical properties. In contrast, at higher coverages, Ni/Pt(111) surfaces begin to act Ni-like, but Pt/Ni(111) surfaces do not act like pure Pt(111) surfaces, most likely due to the lattice mismatch between Ni and Pt.

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