

Ni/Pt(111) Bimetallic Surfaces: Unique Chemistry at Monolayer Ni Coverage

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Abstract: We have utilized the dehydrogenation and hydrogenation of cyclohexene as probe reactions to compare the chemical reactivity of Ni overlayers that are grown epitaxially on a Pt(111) surface. The reaction pathways of cyclohexene were investigated using temperature-programmed desorption, high-resolution electron energy loss (HREELS), and near edge X-ray absorption fine structure (NEXAFS) spectroscopy. Our results provide conclusive spectroscopic evidence that the adsorption and subsequent reactions of cyclohexene are unique on the monolayer Ni surface as compared to those on the clean Pt(111) surface or the thick Ni(111) film. HREELS and NEXAFS studies show that cyclohexene is weakly π -bonded on monolayer Ni/Pt(111) but di- σ -bonded to Pt(111) and Ni(111). In addition, a new hydrogenation pathway is detected on the monolayer Ni surface at temperatures as low as 245 K. By exposing the monolayer Ni/Pt(111) surface to D₂ prior to the adsorption of cyclohexene, the total yield of the normal and deuterated cyclohexanes increases by approximately 5-fold. Furthermore, the reaction pathway for the complete decomposition of cyclohexene to atomic carbon and hydrogen, which has a selectivity of 69% on the thick Ni(111) film, is nearly negligible (<2%) on the monolayer Ni surface. Overall, the unique chemistry of the monolayer Ni/Pt(111) surface can be explained by the weaker interaction between adsorbates and the monolayer Ni film. These results also point out the possibility of manipulating the chemical properties of metals by controlling the overlayer thickness.

1. Introduction

It is well known from the surface science and catalysis literature that the chemical properties of bimetallic surfaces are often different from those of either of the parent metals.^{1–8} For example, Goodman has observed that the Ni/Pt(111) surfaces, with Ni coverages in the monolayer regime, showed higher hydrogenolysis activity than that on either Ni or Pt.⁵ Additionally, Xu and Koel have shown that by adding Sn to Pt(111) surfaces, the resulting (2 × 2)-Sn/Pt(111) surface suppressed the dehydrogenation of cyclohexene on Pt(111).⁴ Another related system, Bi and Pt(111), has also been investigated by Rodriguez and Campbell. They found that by adding Bi, the reactive sites on Pt(111) are titrated since the inert Bi adatoms act as site-blockers for the dehydrogenation reaction.⁶

Previously, we have performed a temperature-programmed desorption (TPD) investigation of the chemical reaction of D₂ on the Ni/Pt(111) bimetallic surfaces.¹ Our results clearly

showed that the reactivity of the bimetallic Ni/Pt surfaces, at near monolayer Ni coverages, is substantially different from that of either Ni(111) or Pt(111). Using D₂ as a probe molecule, we compared the relative binding energies of atomic deuterium by following its recombinative desorption from Pt(111), thick Ni/Pt(111), and a Ni/Pt(111) surface with a monolayer Ni coverage.¹ The main desorption peak of D₂ from the monolayer Ni/Pt(111) surface was at 220 K, which was about 74 K lower than that on Pt(111) and about 154 K lower than that on the thick Ni(111) film. Such a significant reduction in the desorption temperature indicated that the strength of the metal–D bond was much weaker on the monolayer Ni/Pt(111) surface than on either Pt(111) or Ni(111).

To obtain a fundamental understanding of the unique chemical properties of the Ni/Pt(111) surfaces, we have utilized several powerful surface spectroscopies, including high-resolution electron energy loss (HREELS) and near edge X-ray absorption fine structure (NEXAFS), to determine the adsorption and reaction pathways of cyclohexene. There are primarily two reasons for our choice of cyclohexene as the probe molecule. The first one is that the reaction of cyclohexene has been thoroughly studied on the single-crystal surfaces of Pt^{6,10–14} and

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Ni,^{14–16} which would allow us to readily determine any unique adsorption configurations and/or reaction pathways of cyclohexene on the monolayer Ni/Pt(111) surface. Second, using cyclohexene as a probe molecule would also allow us to determine whether the interaction between weakly bonded hydrogen and cyclohexene would lead to a new reaction pathway, the hydrogenation reaction to produce cyclohexane. Our combined TPD, HREELS, and NEXAFS studies have confirmed both hypotheses. From TPD measurements, we have detected the evolution of cyclohexene on the monolayer Ni/Pt(111) surface. Additionally, the amount of hydrogenated products increased with the presence of preadsorbed deuterium. Using HREELS, we have observed the different surface intermediates on Pt(111), monolayer Ni/Pt(111), and the thick Ni(111) film. Last, the polarization-dependence NEXAFS measurements allowed us to confirm the presence of different surface intermediates on the three types of surfaces, as well as to estimate the bonding orientation of the adsorbates on these surfaces.

2. Experimental Section

2.1. Techniques. The ultrahigh-vacuum (UHV) chamber used in the TPD and HREELS studies has been described in an earlier publication.¹⁷ Briefly, it is a three-level chamber that is equipped with a double pass cylindrical mirror analyzer for Auger electron spectroscopy (AES) and photoemission measurements, low-energy electron diffraction (LEED) optics, a quadrupole mass spectrometer (UTI) for TPD measurements, and an LK-3000 HREEL spectrometer. The HREEL spectra reported here are acquired with a primary beam energy of 6.0 eV. Count rates for the elastic peak are typically in the range from 5×10^5 to 2.0×10^6 cps, and the spectral resolution is between 24 and 32 cm^{-1} . For TPD experiments, the cyclohexene exposures were made at 80 K, and the Pt(111) surface was heated at a linear heating rate of 3 K/s.

Carbon K-edge NEXAFS spectra were measured at the National Synchrotron Light Source at the Brookhaven National Laboratory (ExxonMobil U1A beamline). The beamline and the attached UHV chamber have been described in detail previously.¹⁸ NEXAFS spectra were recorded by measuring partial electron yield using a channeltron multiplier located near the sample surface. The UHV chamber is also equipped with an Auger electron spectrometer and a UTI quadrupole mass spectrometer.

The Pt(111) crystal (1.5 mm thick, 12 mm diameter, 99.999% pure) is mounted using standard procedures.¹ The sample temperature is measured by spot welding a type K thermocouple to the back of the Pt(111) crystal. Cyclohexene (Aldrich, 99.99% purity) is further purified by several freeze–pump–thaw cycles prior to use. All other gases used are of research purity and are introduced into the UHV chamber without further purification. The purity of all gases is verified by in-situ mass spectrometry. Gas exposures are reported in langmuirs (1 L = 1.0×10^{-6} Torr s) and are not corrected for differences in gas ionization probabilities.

2.2. Preparation of Clean Pt(111), Ni(111) Film, and Bimetallic Ni/Pt(111) Surfaces. Clean and well-ordered Pt(111) surfaces are obtained by Ne^+ bombardment at 1000 K (3 kV, $\sim 6 \mu\text{A}$ sample current) followed by annealing at 1200 K, and by oxygen treatment, as described previously.¹ The Ni/Pt(111) bimetallic surfaces are prepared by evaporating Ni onto the clean Pt(111) surface. The Ni source consists of a Ni wire (99.999% purity) wrapped around a resistively heated tungsten wire, which is contained in a stainless steel enclosure with an opening of 1 cm in diameter. The concentration of impurities (mainly

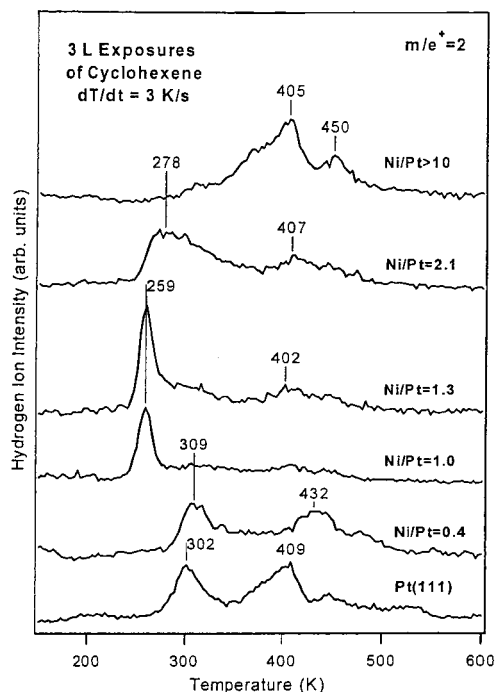


Figure 1. Temperature-programmed desorption spectra of hydrogen obtained following a 3 L exposure of cyclohexene on clean Pt(111), thick Ni(111) film, and Ni/Pt surfaces at ratios 0.4, 1.0, 1.3, and 2.1.

carbon) on the bimetallic surface is just at or below the AES detection limits. Finally, the Pt(111) surface is always held at 600 K during Ni deposition to prevent the adsorption of CO from the UHV background. At 600 K, Ni grows epitaxially on Pt(111), leading to the formation of a Ni(111) film with sharp LEED patterns at higher Ni coverages.¹ The coverage of Ni on Pt(111) is determined by monitoring the Ni(LMM)/Pt(237 eV) Auger peak-to-peak intensity ratios, as described previously.¹

3. Results and Interpretations

3.1. TPD Results. 3.1.1. Cyclohexene on Clean Pt(111) and Ni/Pt(111) Surfaces. The TPD spectra following the adsorption of 3 L of cyclohexene on clean Pt(111) and different Ni/Pt(111) surfaces at various AES ratios are shown in Figures 1 and 2. Figure 1 shows only hydrogen desorption features. For clean Pt(111), H_2 peaks are detected at 302 and 409 K, and several weaker peaks are in the 430–550 K range. The first peak at 302 K corresponds to the initial C–H bond cleavage to form the allyl C_6H_9 and the subsequent breaking of the remaining C–H bonds to form surface benzene.^{6,11} The higher temperature peaks are attributed to the further decomposition of benzene to form surface carbon.^{6,11} When Ni is deposited onto Pt(111) to reach a Ni to Pt AES ratio of 0.4, the general peak shape of the desorption peaks appears similar to that on Pt(111), with the temperatures of the two main peaks increasing slightly to 309 and 432 K. At the Ni/Pt(111) ratios of 1.0 and 1.3, however, dramatic changes are observed in terms of the desorption temperature and peak shape. At these Ni/Pt ratios, a single sharp feature is observed at 259 K. As more Ni is deposited to a Ni/Pt Auger ratio of 2.1, H_2 desorption once again becomes broader and less resolved. After depositing Ni to form an overlayer that has a Ni/Pt Auger ratio above 10, the hydrogen peak shifts to 405 K with a shoulder near 450 K. Overall, these TPD spectra show that at low Ni coverages, the bimetallic surface behaves like Pt; as the Ni/Pt Auger ratio becomes greater than 2, however, the surface begins to behave more like the

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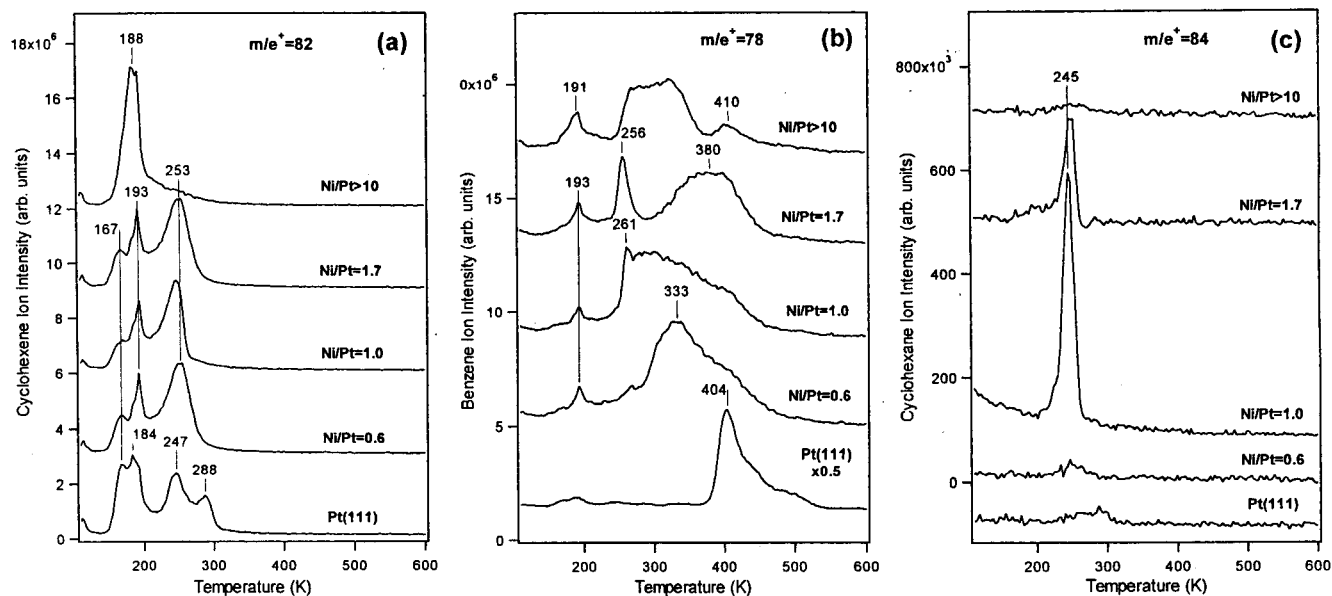
3L Exposures of Cyclohexene, $dT/dt = 3K/s$ 

Figure 2. Temperature-programmed desorption spectra of cyclohexene, benzene, and cyclohexane obtained following a 3 L exposure of cyclohexene on clean Pt(111), thick Ni(111) film, and Ni/Pt surfaces at ratios 0.6, 1.0, and 1.7.

thick Ni(111) film. Finally, the TPD results of the monolayer Ni/Pt(111) surface (Ni/Pt AES ratio of ~ 1.0) show that the chemistry of cyclohexene is significantly different from that of either clean Pt(111) or the thick Ni(111) film.

Figure 2 shows TPD spectra obtained after various Ni/Pt(111) surfaces are exposed to 3 L of cyclohexene. Three masses are monitored: C_6H_{10} (82 amu), C_6H_6 (78 amu), and C_6H_{12} (84 amu). Focusing first on the cyclohexene molecular desorption spectra (Figure 2a), we find four characteristic cyclohexene desorption features, which correspond to the desorption of cyclohexene from multilayers (167 K), from the second layer (184 K), from an agostic bonding state (247 K), and from a di- σ -bonded configuration (288 K).⁶ These assignments were based on previous studies by Rodriguez and Campbell.^{6,11} After depositing Ni to produce a Ni/Pt ratio of 0.6, however, we find that the cyclohexene molecular desorption spectrum changes, with new features appearing at 193 and 253 K. These observations persist for Ni/Pt ratios between 0.6 and 1.7, but are replaced by a single strong desorption peak at 188 K for the thick Ni(111) film.

As shown in Figure 2b, the benzene desorption spectra also vary as the Ni coverage increases. For example, the benzene desorption peak at 404 K on Pt(111) is replaced by a broad peak at 333 K for the surface with a Ni/Pt ratio of 0.6. When the Ni/Pt ratio increases to 1.0, the onset temperature of benzene desorption decreases even lower to 261 K, which is followed by a very broad feature. For the surface with a Ni/Pt ratio of 1.7, the overall shape of the benzene desorption spectrum is remarkably different from those obtained at lower Ni coverages; benzene desorption at this Ni/Pt ratio actually is comprised of a sharp peak at 256 K and a broader feature centered around 380 K. Referring to Figure 2a and b, it is interesting to note that even though the benzene desorption spectrum is different for each Ni/Pt ratio, the corresponding cyclohexene desorption spectrum remains similar throughout these Ni/Pt surfaces. On

the thick Ni(111) film, the benzene desorption spectrum now resembles that obtained for single-crystal Ni(111) surfaces.^{14,19}

Figure 2c shows the thermal desorption spectra obtained by monitoring cyclohexane (84 amu). The spectra corresponding to the clean Pt(111) surface and thick Ni(111) film show almost no $m/e^+ = 84$ peaks, suggesting that no cyclohexane is evolved from these surfaces. For the Ni/Pt(111) ratio of 1.0 surface, however, there is a relatively intense and sharp cyclohexane desorption signal at 245 K. A similar, but less intense cyclohexane peak is also observed for the Ni/Pt(111) surface with an AES ratio of 1.7, indicating that the hydrogenation of cyclohexene occurs on surfaces with Ni/Pt AES ratios between 1.0 and 1.7.

3.1.2. Coadsorption of D_2 and Cyclohexene on the Monolayer Ni/Pt(111) Surface. Figure 3 shows the TPD spectra obtained after adsorbing 0.5 L of D_2 prior to the 3 L exposure of cyclohexene. In this experiment, masses 85 amu ($C_6H_{11}D$) and 86 amu ($C_6H_{10}D_2$) are monitored in addition to mass 84 amu (C_6H_{12}). As reported earlier, the 0.5 L exposure of D_2 on monolayer Ni/Pt(111) corresponds to an atomic D coverage of 37% of saturation.²⁰ The TPD results show that by coadsorbing deuterium with cyclohexene, significantly more hydrogenated products are produced. Additionally, the TPD peaks of the various cyclohexane products become broader, and the onset of desorption occurs at lower temperatures. While one expected the evolution of mass 85 and mass 86 cyclohexanes, it is interesting to note that the presence of surface deuterium also aided in the desorption of mass 84 cyclohexane. In the Discussion section we will quantify the effect of surface deuterium on the yield of cyclohexane.

3.2. HREEL Studies. HREEL spectra for cyclohexene adsorbed on clean Pt(111) and the Ni/Pt(111) surfaces are

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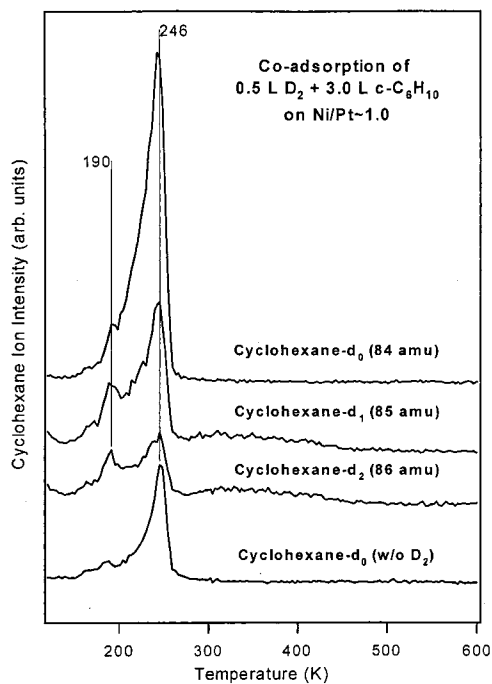


Figure 3. Temperature-programmed desorption spectra of cyclohexane products (84, 85, and 86 amu) obtained following the coadsorption of 0.5 L of D_2 and 3 L of cyclohexene on the monolayer Ni/Pt(111) surface.

described in this section. The exposures of $c\text{-C}_6\text{H}_{10}$ are made with the crystal temperature at 80 K; the adsorbed layer is then heated to the indicated temperatures and cooled immediately before the HREEL spectra are recorded. The temperatures were chosen on the basis of the TPD experiments.

3.2.1. Cyclohexene on the Pt(111) Surface and the Ni(111)

Film. To provide a basis for comparison, we will first assign the vibrational spectra of cyclohexene on the clean Pt(111) surface and thick Ni(111) film. The chemistry of cyclohexene on these two surfaces is considerably different, as will be shown below, and is also distinctly different from that observed on the monolayer Ni/Pt(111) surface. Figure 4 shows a comparison of HREEL spectra recorded after exposing clean Pt(111) to 3 L of cyclohexene. Figure 4a–e shows the HREEL spectrum at 80 K and after heating to 200, 250, 300, and 450 K, respectively. The spectra corresponding to 80 K is characteristic of di- σ -bonded C_6H_{10} via the $C=C$ bond of cyclohexene, as indicated by the absence of $\delta(C=C)$ at $\sim 740\text{ cm}^{-1}$, $\nu(C=C)$ at $\sim 1600\text{ cm}^{-1}$, and $\delta(=CH)$ at $\sim 3050\text{ cm}^{-1}$. After heating to 200 K, no major changes are observed aside from the disappearance of the skeletal distortion mode at 643 cm^{-1} . After heating to 250 K, we observe the following vibrations: $\nu(C-C)$ at 819 and 893 cm^{-1} , $\nu(C-C) + \rho(CH_2)$ at 1076 cm^{-1} , $\omega(CH_2)$ at 1224 and 1285 cm^{-1} , $\delta(CH_2)$ at 1434 cm^{-1} , and $\nu(CH)$ at 2861 and 2922 cm^{-1} . While the HREEL spectrum at 300 K exhibited small changes in peak energy and relative intensities, no major deviations from the 250 K spectrum are recorded. By comparing Figure 4c and d with previously studied cyclohexene–metal systems,^{6,10,11,15,16,21} we can conclude that at 250 and 300 K, cyclohexene decomposes to form a C_6H_9 allyl intermediate. Last, heating to 450 K changed the HREEL spectrum considerably due to the conversion of the C_6H_9 intermediate to benzene. The

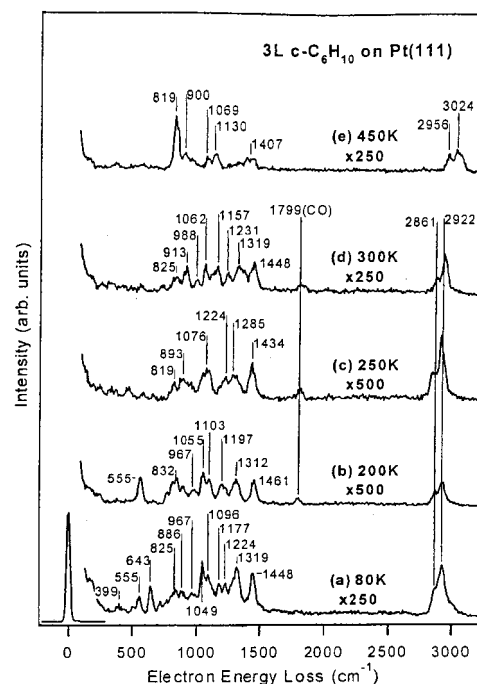


Figure 4. HREEL spectra monitoring the thermal decomposition of 3 L of C_6H_{10} on clean Pt(111) following adsorption at 90 K.

major modes of Figure 4e are at 819, 900, 1069, 1130, 1407, 2956, and 3024 cm^{-1} , which correspond reasonably well with those reported for chemisorbed benzene.^{9,10,15,16} The mode assignments for molecular cyclohexene and the C_6H_9 allyl intermediate, as well as surface benzene, are provided in Tables 1 and 2.

When cyclohexene is exposed to a thick Ni(111) layer, the eventual product is benzene as well, but the temperature required for the conversion is much lower than that on the Pt(111) surface. Figure 5 shows HREEL spectra recorded after exposing a thick Ni(111) layer to 3 L of cyclohexene at 80 K, and then heating to the indicated temperatures. At 80 K, the detection of the characteristic skeletal distortion mode at 642 cm^{-1} and the $\delta(C=C)$ mode at 724 cm^{-1} ²¹ indicates that molecular cyclohexene species are still intact. After heating to 200 K, however, we already find significant changes in the spectrum that are consistent with the conversion of cyclohexene to benzene. Specifically, the intense mode at 757 cm^{-1} , with an accompanying shoulder at 819 cm^{-1} , is characteristic of benzene on Ni(111) surfaces; using the Herzberg notation,²² these modes are ascribed to the ν_4 and ν_{11} modes of benzene, which are concerted out-of-plane deformations of the $C-H$ bonds. Further heating to 250 and 300 K resulted in no significant changes. Furthermore, the near absence of $\nu(CH)$ modes indicates that the benzene ring is approximately parallel to the surface, which corresponds well with prior investigations on Ni(111) single crystals.^{15,16} This observation will be confirmed by the NEXAFS experiments. By combining HREELS results with the TPD measurements (Figure 2), we can conclude that the evolution of benzene from the thick Ni(111) film is desorption-limited. Last, at 450 K, only the $\gamma(C-H)$ (764 cm^{-1}) and the CO (1711 cm^{-1}) features remain on the surface.

3.2.2. Cyclohexene on the Monolayer Ni/Pt(111) Surface. Figure 6 shows HREEL spectra obtained after exposing a

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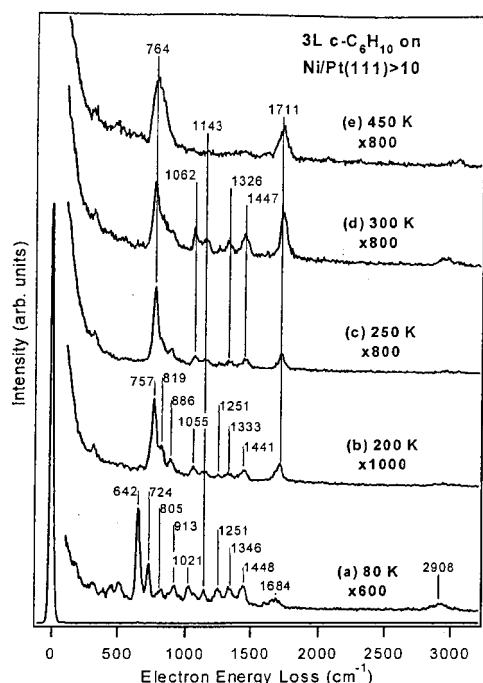
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Table 1. Vibrational Assignments for Cyclohexene on Clean Pt(111) and Monolayer Ni/Pt(111)

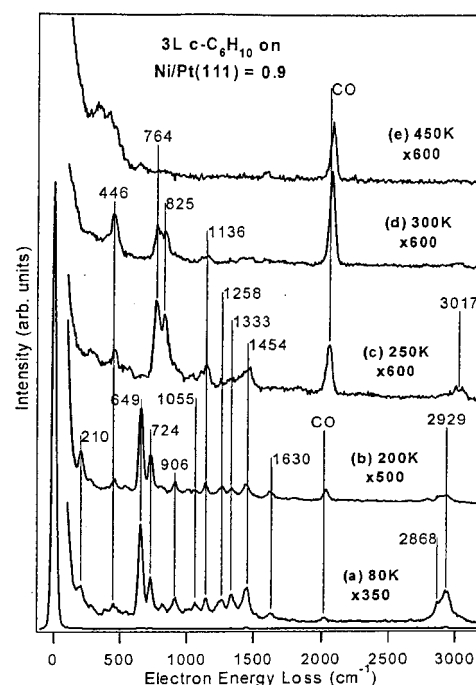
mode	liquid ³⁰	α -bonded C ₆ H ₈ on Pt(111) [this work]	α -bonded C ₆ H ₈ on Pt(111) ¹¹	π -bonded C ₆ H ₁₀ on monolayer Ni/Pt(111)
ring deformation	175, 280, 393, 452			446
ν (M-C)		555(?)		
skeletal distortion	640, 670			649
δ (C=C)	720			724
ν (C-C)	810, 905, 917	832, 967	840, 890	906
ν (C-C) + ρ (CH ₂)	1038	1055	1065	
ω (CH ₂) rock	1138	1103	1130	1136
ω (CH ₂) twist	1241, 1264	1197	1300	1258
ω (CH ₂) wag	1321-1350	1312	1370	1333
δ (CH ₂) scissors	1438-1456	1461	1435	1454
ν (C=C)	1653			1630
ν (-C-H)	2840-2993	2861, 2922	2930	2929
ν (=C-H)	3026, 3065			

Table 2. Vibrational Assignments for Chemisorbed Benzene on Ni(111) and the Thick Ni(111) Film

mode	free benzene ³¹	chemisorbed C ₆ H ₆ on Ni(111) ¹⁶	chemisorbed C ₆ H ₆ on thick Ni(111) film
ν (M-C)			
γ (C-H)	673, 845	745	757, 819
ν (C-C)	993	845	886
δ (C-H)	1038, 1150	1110	1055, 1143
δ (C-C)	1309	1320	1333
ν (C-C) + δ (C-C)	1486	1420	1441
ν (C-C)	1596		
ν (C-H)	3074	3020	

**Figure 5.** HREEL spectra monitoring the thermal decomposition of 3 L of C₆H₁₀ on the thick Ni(111) film following adsorption at 90 K.

surface, with a Ni/Pt(111) AES ratio of 0.9, to 3 L of cyclohexene and then heating to the same temperatures as in Figures 4 and 5. The spectrum at 80 K is indicative of weakly π -bonded cyclohexene, with the characteristic skeletal deformation, δ (C=C), and ν (C=C) modes at 649, 724, and 1630 cm⁻¹, respectively.^{21,23} Further heating to 200 K produced no signifi-

**Figure 6.** HREEL spectra monitoring the thermal decomposition of 3 L of C₆H₁₀ on the monolayer Ni/Pt(111) (AES ratio ~0.9) surface following adsorption at 90 K.

cant changes, indicating that cyclohexene remains molecularly adsorbed to at least this temperature. At 250 K, however, significant spectral changes are observed: (1) The two modes at 649 and 724 cm⁻¹ are replaced by a pair of features at 757 and 825 cm⁻¹, (2) the ν (C=C) mode at 1630 cm⁻¹ disappears, and (3) the ν (C-H) modes shift to >3000 cm⁻¹. Overall, these changes are consistent with the dehydrogenation of cyclohexene to form benzene, and the modes at 757 and 825 cm⁻¹ can be assigned to the ν_4 and ν_{11} modes of benzene.²² Interestingly, the spectrum in Figure 6c does not show any spectral features characteristic of cyclohexene even though the TPD results show a relatively intense $m/e^+ = 84$ signal at 245 K for this surface. This observation suggests that the evolution of cyclohexene from the monolayer Ni/Pt(111) surface is reaction-limited rather than desorption-limited. Further heating to 300 K results in a spectrum that is similar to the one at 250 K, which corresponds well with TPD results showing that benzene does not completely desorb until ~400 K on this surface. By 450 K, no detectable traces of cyclohexene intermediates remain, and the only other surface species observed is CO from the chamber background.

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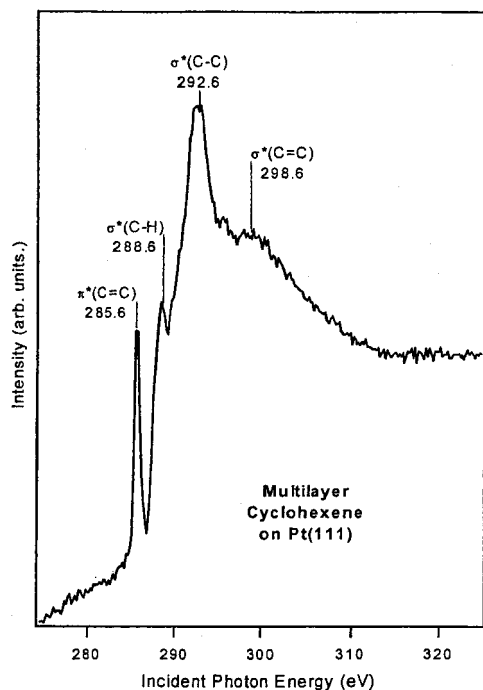


Figure 7. Normal NEXAFS spectra obtained after exposing clean Pt(111) to multilayer C_6H_{10} at 90 K.

3.3. NEXAFS Studies of Cyclohexene on Pt(111) and Ni/Pt(111) Surfaces. Figure 7 shows the four major features in the NEXAFS spectrum of multilayer cyclohexene on Pt(111). Similar to that described earlier by Stohr,²⁴ the NEXAFS features can be assigned as follows: (1) The first is a sharp peak at 285.6 eV, which corresponds to a π^* excited state of the C=C bond. (2) The second peak is also sharp, at 288.6, and can be assigned to the $\sigma^*(C-H)$ excited state. (3) The next two relatively broad peaks at 292.6 and 298.6 eV are attributed to the $\sigma^*(C-C)$ and $\sigma^*(C=C)$ excited states, respectively.

Figure 8 shows NEXAFS spectra recorded after exposing Pt(111), thick Ni(111) film, and monolayer Ni/Pt(111) to 3 L of cyclohexene and then heating to 200 K; both normal (90° with respect to the surface) and glancing (30° with respect to the surface) incidence spectra are shown. For the Pt(111) surface, the observation of a broad and relatively weak $\pi^*(C=C)$ resonance at 285.6 eV is typical for hydrocarbons that are di- σ -bonded to the surface via the C=C moiety. In addition, the detection of the characteristic features of the C6 ring, the $\sigma^*(C-H)$ feature at 288.6 eV and the $\sigma^*(C-C)$ at 292.6 eV, suggests that the surface species are di- σ -bonded cyclohexene intermediates. Overall, NEXAFS results of cyclohexene on Pt(111) are consistent with the conclusions from the HREELS results. In addition, the polarization dependence of the intensity of the 285.6 eV feature suggests that the C=C bond is nearly parallel to the Pt(111) surface.

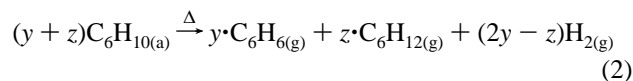
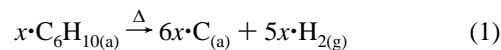
For the thick Ni(111) film, there are two features at 285.6 and 287.2 eV in the glancing incidence, which are much weaker in the normal incidence spectrum. The presence of these two features is typically observed for benzene lying relatively flat on a metal surface^{24,25} and can be attributed to transitions from the carbon 1s level to the π_1^* and π_2^* levels. Other spectral features, such as the $\sigma^*(C-H)$ feature at 288.6 eV and the σ^* -

(C-C) feature at 293.4 eV, are also characteristic of benzene. These results support the assertion that cyclohexene is converted to benzene on the thick Ni(111) film by 200 K. Overall, these NEXAFS spectra are in excellent agreement with the conclusions derived from the HREELS results.

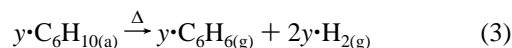
For cyclohexene on the monolayer Ni/Pt(111) surface, NEXAFS results are distinctly different from those on either Pt(111) or the thick Ni(111) film. An intense and very sharp $\pi^*(C=C)$ feature is observed at 286.0 eV. Additional features, at 288.8, 292.6, and 299 eV, are attributed to $\sigma^*(C-H)$, $\sigma^*(C-C)$, and $\sigma^*(C=C)$ of cyclohexene, respectively. The observation of a sharp and intense π^* feature at 286.0 eV supports the conclusions from HREELS studies that cyclohexene is molecularly and weakly bonded to the monolayer Ni/Pt(111) surface at 200 K. In addition, the polarization dependence of this π^* feature indicates that the C=C bond of molecularly adsorbed cyclohexene is nearly parallel to the surface.

4. Discussion

4.1. Reaction Pathways and Product Selectivity. The observed reaction pathways of cyclohexene on Pt(111), monolayer Ni/Pt(111), and thick Ni/Pt(111) surfaces can be summarized by the following equations; these equations represent the net reactions of cyclohexene on different surfaces.



Reaction 1 indicates the complete dissociation of cyclohexene, whereas reaction 2 involves both the dehydrogenation and the hydrogenation of cyclohexene to produce benzene and cyclohexane, respectively. Since no cyclohexane is observed on the Pt(111) surface, the coefficient z is 0 on this surface, and eq 2 simplifies to



The values of x and y were previously obtained to be 0.03 and 0.09 cyclohexene molecules per Pt atom, respectively.¹³ The overall activity on clean Pt(111) is therefore $x + y = 0.12$ cyclohexene molecules per Pt atom, with 75% of the cyclohexene dehydrogenating to form gas-phase benzene; this selectivity is similar to the value of 75–77% that was previously reported by Rodriguez and Campbell.⁶

The product selectivity for cyclohexene on the thick Ni(111) film is determined simply by comparing the relative TPD peak areas from the thick Ni(111) film to that from the clean Pt(111) surface. Using the relationships shown below, we calculated that the coefficients x and y for the thick Ni(111) film are 0.085 and 0.054 molecules per Pt atom, respectively, by using the following relationships:

$$\frac{\text{area}_{\text{benzene}}^{\text{thick Ni(111) film}}}{\text{area}_{\text{benzene}}^{\text{Pt(111)}}} = 0.6 \Rightarrow y_{\text{thick Ni(111) film}} = 0.054 \quad (4)$$

$$\frac{\text{area}_{\text{hydrogen}}^{\text{thick Ni/Pt}}}{\text{area}_{\text{hydrogen}}^{\text{Pt(111)}}} = 1.61 \Rightarrow (5x + 2y)_{\text{thick Ni(111) film}} = 0.53 \Rightarrow$$

$$x = 0.085 \quad (5)$$

(24) Stohr, J. *NEXAFS Spectroscopy*; Springer-Verlag: New York, 1992 and references therein.

(25) Liu, A. C.; Friend, C. M. *J. Chem. Phys.* **1998**, *89*, 4396.

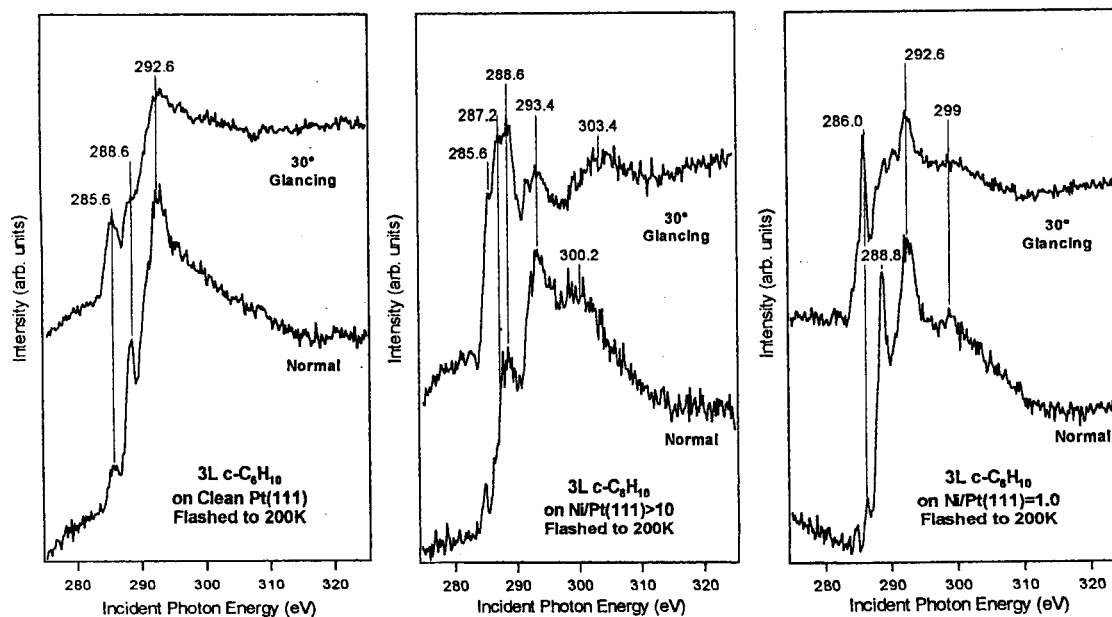


Figure 8. Normal and glancing NEXAFS spectra obtained after exposing clean Pt(111), thick Ni(111) film, and monolayer Ni/Pt(111) to 3 L of C_6H_{10} at 90 K and flashed to 200 K. The grazing and normal spectra refer to measurements with the crystal surface at a glancing (30°) and normal (90°) angle with respect to the incident photon beam.

Table 3. Product Yields of Cyclohexene on the Clean Pt(111), Monolayer Ni/Pt(111), and Thick Ni/Pt(111) Surfaces

surface	C_6H_6 – activity per metal atom (% selectivity)	C_6H_{12} – activity per metal atom (% selectivity)	$C + H_2$ – activity per metal atom (% selectivity)	overall activity
Pt(111) ¹³	0.09 per Pt (75)	~0 per Pt (0)	0.03 per Pt (25)	0.12
monolayer Ni/Pt(111)	0.086 per Pt (89)	0.009 per Pt (9.3)	0.002 per Pt (1.7)	0.097
thick Ni/Pt(111)	0.044 per Ni (39)	~0 per Ni (0)	0.068 per Ni (61)	0.112

To normalize the activity on the per Ni atom basis, however, one needs to account for the differences in the density of Ni(111) and Pt(111). After including this factor (density_{Ni}/density_{Pt} = $r_{Pt}^2/r_{Ni}^2 = 1.39^2/1.25^2 = 1.24$), x and y become 0.044 and 0.068, respectively. The overall activity on thick Ni(111) film is therefore 0.112 cyclohexene molecules per Ni atom, with approximately 39% of the cyclohexene dehydrogenating to produce gas-phase benzene.

On the monolayer Ni/Pt(111) surface, the coefficient y can also be obtained by comparing the TPD peak areas from the monolayer surface to that from the clean Pt(111) surface.

$$\frac{\text{area}_{\text{benzene}}^{\text{monolayer Ni/Pt}}}{\text{area}_{\text{benzene}}^{\text{Pt(111)}}} = 0.95 \Rightarrow y_{\text{monolayer Ni/Pt}} = 0.086 \quad (6)$$

The calculation of x is less straightforward, however, as we first need to account for the formation of cyclohexane, z . To determine the amount of hydrogenated product on the monolayer Ni/Pt(111) surface, it is necessary to estimate the TPD area ratio of C_6H_{12}/C_6H_6 . By taking into consideration the different ion gauge sensitivity factors for C_6H_{12} (6.4) and C_6H_6 (5.9),²⁶ we obtain the mass spectrometer intensity ratio of C_6H_{12}/C_6H_6 to be ~0.36 at equal pressures of C_6H_{12} (6.4×10^{-8} Torr) and C_6H_6 (5.9×10^{-8} Torr). After accounting for this ratio, the corrected C_6H_{12}/C_6H_6 TPD area ratio is 0.108, which in turn gives the value of $z = 0.009$. The value x can then be calculated

by the following relationships:

$$\frac{\text{area}_{H_2}^{\text{monolayer Ni/Pt}}}{\text{area}_{H_2}^{\text{Pt(111)}}} = 0.52 \Rightarrow 2y - z + 5x = 0.17 \Rightarrow x = 0.002$$

From these calculations, the overall activity on this bimetallic surface is $x + y + z = 0.097$ cyclohexene molecules per Pt atom, with 89, 9, and 2% of the cyclohexene going to benzene, cyclohexane, and complete decomposition, respectively. For monolayer Ni/Pt(111) we present the surface activity on the basis of per Pt atom instead of per Ni atom. This is because we do not know whether the Ni density is similar to that of Pt(111) or Ni(111) at the monolayer Ni coverage. A summary of the above results is provided in Table 3.

In section 3.1.2 we examined the effect of preadsorbed D_2 on the formation of hydrogenated products. The results from the 0.5 L of D_2 and 3 L of C_6H_{10} coadsorption experiments showed significantly more cyclohexane production from the monolayer Ni/Pt surface. By comparing TPD peak areas, it is determined that the desorption of C_6H_{12} increased from 0.009 to 0.026 cyclohexene molecules per Pt atom. Relatively large quantities of deuterated cyclohexane products are also detected. By comparing the TPD areas of deuterated cyclohexane to that of C_6H_{12} , the yields of $C_6H_{11}D_1$ and $C_6H_{10}D_2$ are estimated to be 0.007 and 0.013 cyclohexene molecules per Pt atom, respectively. The total yield of cyclohexane products (C_6H_{12} , $C_6H_{11}D_1$, and $C_6H_{10}D_2$) is 0.046 cyclohexene per Pt atom, which represents a 5-fold increase in the hydrogenation activity. These results are summarized in Table 4.

(26) Table 17: Ionization Probability Table. *Product and Vacuum Technology Reference Book*; Leybold Vacuum Products, Inc.: Export, PA, 1994; pp 18–103.

Table 4. Cyclohexane Yields from the Coadsorption of D₂ and C₆H₁₀ on Monolayer Ni/Pt(111)

products (activity per Pt atom)	3 L of C ₆ H ₁₀	coadsorption of 1 L of D ₂ and 3 L of C ₆ H ₁₀
C ₆ H ₁₂	0.009	0.026
C ₆ H ₁₁ D ₁	0	0.013
C ₆ H ₁₀ D ₂	0	0.007

4.2. Unique Chemistry on Monolayer Ni/Pt(111). From the TPD, HREELS, and NEXAFS results presented above, it is clear that the monolayer Ni/Pt(111) surface is characterized by chemical properties that are distinctly different from those of either Pt(111) or the thick Ni(111) film. Our results of the reaction pathways of cyclohexene on Pt(111) and thick Ni(111) film are consistent with previous studies on Pt^{6,9–14,29,30} and Ni;^{14–16,27,28} in the remainder of the discussion we will focus on the unique chemistry on the monolayer Ni/Pt(111) surface.

The reaction pathway of cyclohexene on the monolayer Ni surface is drastically different from Pt(111) or thick Ni(111) film in several aspects: (1) Both HREELS (Figure 6) and NEXAFS (Figure 8) results reveal that cyclohexene is weakly π -bonded to the monolayer Ni/Pt(111) surface at temperatures up to 200 K. (2) TPD measurements (Figures 1 and 2) detect several gas-phase products at low temperatures, cyclohexane at \sim 245 K, H₂ at \sim 259 K, and the desorption of benzene at an onset temperature of \sim 261 K. (3) The product selectivity (Tables 3 and 4) is approximately 9% for cyclohexane and 89% for gas-phase benzene, with only a negligible amount (\sim 2%) of adsorbed cyclohexane undergoing complete decomposition to produce atomic carbon and hydrogen. (4) The overall surface activity (Tables 3 and 4), as compared in the common unit of number of cyclohexene molecules undergoing reactions on a per metal atom basis, is lower on monolayer Ni (0.097 per Pt atom) than on the thick Ni(111) film (0.112 per Ni atom).

By comparing to the thick Ni(111) film, the unique chemical properties of the monolayer Ni/Pt(111) surface can be attributed to that fact that *both* unsaturated hydrocarbons *and* atomic hydrogen are bonded more weakly on the monolayer Ni surface. For example, the observation that the benzene intermediates undergo either hydrogenation or dehydrogenation, instead of complete decomposition, is an indication of a weaker interaction between adsorbed benzene and the monolayer Ni surface. Furthermore, the TPD detection of the low-temperature cyclohexane product on monolayer Ni/Pt(111) is most likely resulting from the interaction of weakly adsorbed atomic hydrogen with weakly π -bonded cyclohexene. This is consistent with the hydrogenation studies on Pt(111) by Somorjai and co-workers,^{29,30} where weakly π -bonded species have been identified

(27) Son, K.-A.; Gland, J. L. *J. Phys. Chem. B* **1997**, *101*, 3540. Son, K.-A.; Mavrikakis, M.; Gland, J. L. *J. Phys. Chem.* **1995**, *99*, 6270.

(28) Tjandra, S.; Zaera, F. *J. Catal.* **1996**, *164*, 82.

(29) Su, X.; Kung, K.; Lahtinen, J.; Shen, R. Y.; Somorjai, G. A. *Catal. Lett.* **1998**, *54*, 9.

(30) Su, X.; Kung, K. Y.; Lahtinen, J.; Shen, Y. R.; Somorjai, G. A. *J. Mol. Catal. A* **1999**, *141*, 9. McCrea, K. R.; Somorjai, G. A. *J. Mol. Catal. A* **2000**, *163*, 43.

as precursor states for hydrogenation reactions. The involvement of weakly adsorbed hydrogen in the hydrogenation of cyclohexene is also consistent with the model proposed by Newton and Campbell,³¹ which attributes more weakly bonded hydrogen as the greater thermodynamic driving force for the hydrogenation of methylcyclohexene.

In summary, the results in the current paper clearly demonstrate the unique chemistry on the monolayer Ni/Pt(111) surface, which is most likely related to the fact that the bonding between adsorbates and the monolayer Ni surface is weaker than that on either Pt(111) or the thick Ni(111) film. This is also confirmed in our recent studies of hydrodesulfurization of thiophene on monolayer Ni/Pt(111).²⁰ At present we do not completely understand why the bonding is weaker on the monolayer Ni/Pt(111) surface. We are in the process of investigating the chemistry of monolayer Ni on the substrates of two other closely packed surfaces, W(110) and Ru(0001), to determine the role of the substrates. Systematic NEXAFS and photoemission studies of Ni overlayers are also underway to determine whether the unique chemistry is related to alterations in the electronic and/or structural properties at the monolayer Ni thickness.

5. Conclusions

By using the dehydrogenation and hydrogenation of cyclohexene as chemical probes, our results provided conclusive spectroscopic evidence demonstrating the unique chemical properties of the monolayer Ni/Pt(111) surface. Unlike either the Pt(111) or the thick Ni(111) film, cyclohexene molecules are weakly π -bonded to the monolayer Ni surface at a temperature up to 200 K. The unique chemistry is also reflected by the desorption of benzene and hydrogen, as well as by the detection of a new gas-phase cyclohexane product, at temperatures between approximately 245–261 K. The product selectivity to gas-phase cyclohexane is approximately 9% on the monolayer Ni/Pt(111) surface, and the cyclohexane yield is increased by a factor of 5 by exposing the monolayer Ni to D₂ prior to the adsorption of cyclohexene. Overall, our results suggest that the unique chemistry is related to the weaker bonding between adsorbates and the monolayer Ni surface. More detailed studies are underway to determine the differences in the electronic and structural properties between monolayer Ni and thick Ni films.

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(31) Newton, M. A.; Campbell, C. T. *Z. Phys. Chem.* **1997**, *198*, 169.