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SURFACE SCIENCE LETTERS

Orientation of nickelocene on Ag(100)

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Abstract: High-resolution electron-energy-loss spectroscopy has been used to study the molecular adsorption of nickelocene, $\text{Ni}(\text{C}_5\text{H}_5)_2$, on Ag(100). Results indicate that at up to one monolayer coverage, nickelocene adsorbs molecularly with its axis approximately perpendicular to the surface. At very high coverages, the molecular axis is not exclusively oriented along the surface normal. This is possibly due to randomization of the metallocene orientation as multilayers are formed.

Keywords: Ag(100), electron-energy-loss spectroscopy, nickelocene

1. Introduction

Recently, there have been several studies of adsorbed metallocenes, primarily as a result of their potential use as source molecules for the selective area deposition of metals on surfaces ([1–7]; D. Welipitiya, C. Waldfried, P. A. Dowben, I. Goblukoglu, B. Robertson, in preparation). Determination of the dominant interactions between a particular metallocene and the surface is essential for understanding how the metallocene decomposes and deposits metal on a surface. A key part of this understanding is the orientation of the metallocene–surface system. The few studies that have focused on this piece of information, though carefully performed, have generally required several monolayers to multilayers of the metallocene in their experimental conditions ([5, 6, 7]; C. M. Woodbridge, D. L. Pugmire, M. A. Langell, in preparation). To our knowledge, no studies of nickelocene

on any surface using high-resolution electron-energy-loss spectroscopy (HREELS) have been performed. HREELS is an ideal tool for determining adsorbate geometry because of its sensitivity to surface symmetry and orientation of adsorbates. This paper reports the results for nickelocene (NiCp_2 , where Cp = cyclopentadienyl) on the Ag(100) surface.

2. Experimental

A silver single crystal oriented along the (100) plane was mounted on a manipulator capable of resistive heating and liquid-nitrogen cooling. The temperature of the sample was monitored with a type-K thermocouple (chromel–alumel). The sample was cleaned by repeated cycles of sputtering with Ar^+ (0.5 keV and 25 mA) at 623 K for 15 min followed by annealing at

673 K for 20 min. The sample was determined to be clean as judged by the absence of carbon or any other contaminant signal in AES. The surface was cooled to 135 K before exposure to NiCp₂. This is well below the desorption temperature for nickelocene on Ag(100), observed at approximately 212 K [7]. The sample surface was then dosed by the admission of nickelocene vapor into the chamber through a standard leak valve with a needle doser that concentrated the vapor in the vicinity of the Ag(100) crystal. A series of doses was performed by opening the leak valve to allow the background pressure in the system to increase by 0.1×10^{-9} Torr and holding at that pressure for 3 s. Sequential dosing performed in this manner led to very reproducible increases in nickelocene surface coverage, as measured by X-ray photoelectron spectroscopic (XPS) C 1s/Ag 3d_{5/2} intensity ratios. Absolute exposures were calibrated for dosage time by setting the monolayer coverage to an exposure of 10 Langmuirs (1 Langmuir = 1×10^{-6} Torr·s) of nickelocene, in agreement with saturation exposures reported in previously reported studies on Ag(100) [7]. The XPS data are described in more detail below.

The high-resolution electron-energy-loss spectra were obtained using a LK-2000 spectrometer. Electrons were incident to the surface at 60° from the surface normal with a primary beam energy of 3.77 eV and a beam current of 90 pA. The typical resolution (FWHM) for the spectra obtained ranged from 4 to 5 meV. XPS was performed with MgK α radiation (1253.6 eV) and a Physical Electronics model 15-225G double-pass cylindrical mirror analyzer. Pass energies of 50 eV were employed for the carbon 1s and silver 3d regions, and 100 eV for the nickel 2p region. The binding energies were calibrated by reference to the substrate 3d_{5/2} transition taken to have a value of 367.9 eV.

3. Results and Discussion

XPS were taken of the Ag(100)–nickelocene adsorbate complex as a function of nickelocene exposure. The carbon 1s region yielded a single peak at 284.7 eV, with a binding energy independent of the surface coverage. Nickel 2p values were 854.6 and 871.7 eV for the 2p_{3/2} and

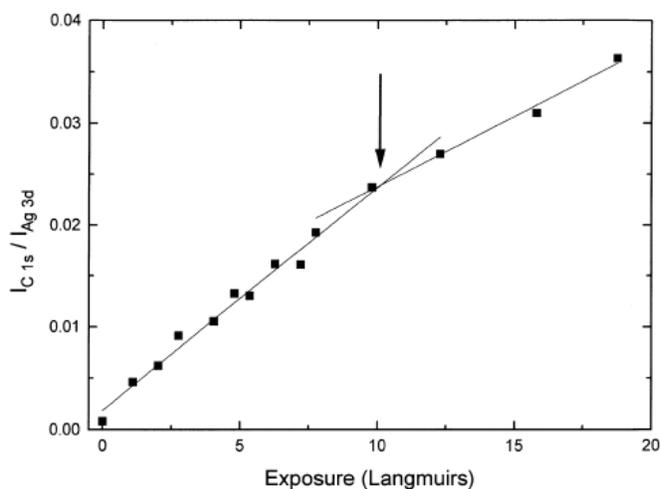


Figure 1. Ratio of C 1s/Ag 3d intensities as determined by XPS as a function of nickelocene exposure. The arrow indicates the approximate completion of one monolayer on Ag(100).

2p_{1/2} transitions, respectively. The binding energies and C 1s/Ni 2p_{3/2} intensity ratios indicate that the metal nominally retains its oxidation state of Ni²⁺ and has the correct stoichiometric ratio of 10 C/1 Ni, in agreement with the molecular adsorption found in HREELS and described below. Figure 1 shows the C 1s/Ag 3d_{5/2} intensity ratio as a function of sample dosage. A clear break in rate of carbon uptake is observed reproducibly at the point indicated by the arrow in Figure 1, and this is attributed to completion of the first nickelocene monolayer. The first monolayer of nickelocene was previously reported [7] to saturate on Ag(100) after 10 Langmuirs (L) under similar substrate temperature and dosing conditions.

Assuming a staggered ring configuration, the free nickelocene molecule belongs to the D_{5d} point group. In this point group, modes with either A_{2u} or E_{1u} symmetries are IR-active. Modes with A_{2u} character have dipoles polarized in the z-direction, along the molecular axis, and modes with E_{1u} character are polarized in the x, y-plane. These are modes that, depending on the orientation of the molecule with respect to the surface, are predicted by the surface dipole selection rule to be dipole active. If nickelocene adsorbed with the molecular axis perpendicular to the surface, the A_{2u} modes would be dipole-active, and the E_{1u} modes would not. At the other

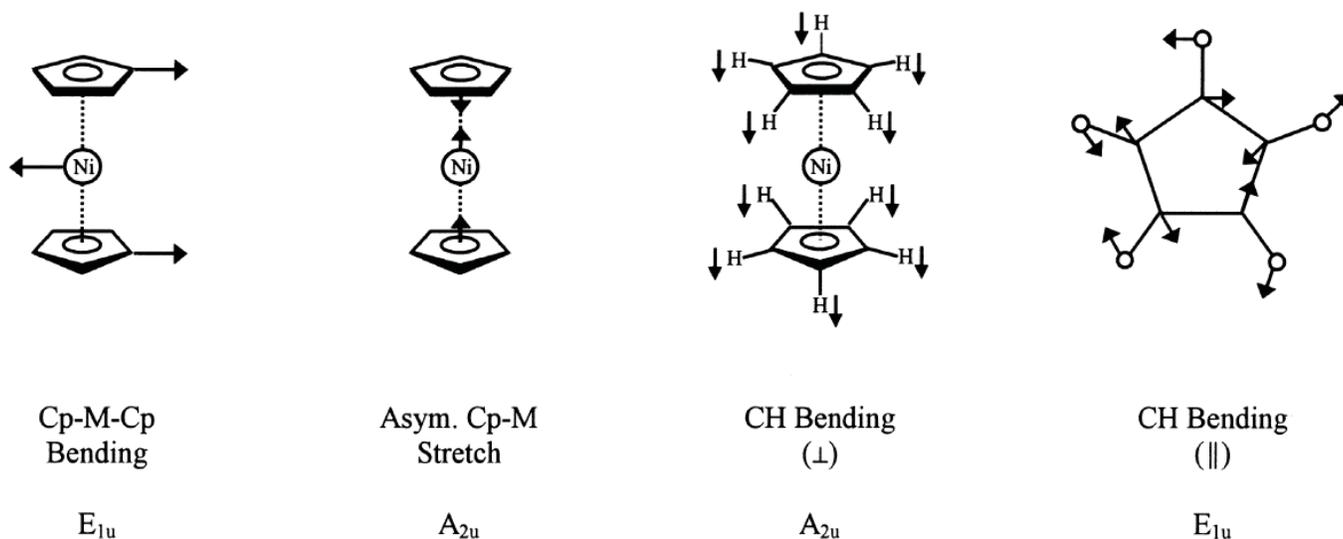


Figure 2. The four relevant modes of nickelocene showing the molecular motion and the symmetries.

extreme, if the molecules adsorbed so that the cyclopentadienyl rings were perpendicular to the surface, only the E_{1u} modes could be dipole-active. With the molecule adsorbed at any angle between these extremes, both the A_{2u} and E_{1u} modes could exhibit dipole scattering.

A complete and accurate assignment of all the losses observed in the spectra will require the deuterated NiCp_2 on $\text{Ag}(100)$ HREEL spectrum, which is currently being investigated in our lab. However, there are four easily assigned modes (Figure 2) that can be used to determine unequivocally the orientation of the nickelocene molecule. The first is the ring-metal-ring bending mode, which has E_{1u} symmetry. The second is the asymmetric ring-metal-ring stretch, which has A_{2u} symmetry. The third mode is a C-H bending, perpendicular to the plane of the rings, with A_{2u} symmetry. The fourth is another C-H bending mode occurring in the plane of the cyclopentadienyl rings, with E_{1u} symmetry. The solution IR energies for these modes are 15.5, 44.0, 95.9, and 124.0 meV, respectively [8].

The on-specular HREEL spectrum of one monolayer of NiCp_2 on $\text{Ag}(100)$ is shown as the top spectrum of Figure 3. The modes are largely unperturbed relative to gas phase nickelocene, indicating that little rehybridization takes place at 135 K. Both modes with A_{2u} symmetry are seen as intense losses occurring very close to their respective solution IR values. Table 1 shows the experimental energies of these losses. The ring-metal-ring

bending mode (E_{1u}) that should be seen near the solution IR value of 15.5 meV [8] is not present. The C-H bending mode with E_{1u} symmetry appears at 124.4 meV with little intensity. The off-specular spectrum (bottom in Figure 3) shows a substantial decrease in the intensity of the A_{2u} modes when compared with the spectrum taken in the specular direction. The E_{1u} mode has the same intensity in both spectra. The dipole activity of only the A_{2u}

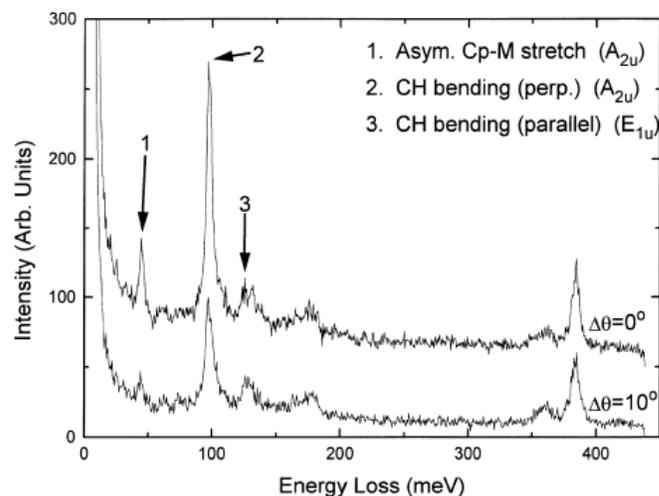


Figure 3. Electron-energy-loss spectra for one monolayer of nickelocene on $\text{Ag}(100)$ at 135 K. The A_{2u} modes are dipole-active, and the E_{1u} modes are nearly undetectable. Both spectra are shown on the same scale.

Table 1.
Dominant energy loss modes in the HREEL spectra of nickelocene

Mode	Symmetry	Solution IR (meV) ^a	1 ML (meV) ^b	High coverage (meV) ^b
Cp-M-Cp bending	E_{1u}	15.5	Not observed	16.5
Asym. Cp-M stretch	A_{2u}	44.0	44.5	44.5
CH bending (\perp)	A_{2u}	95.9	96.9	96.9
CH bending (\parallel)	E_{1u}	124.0	124.4	124.4

Fundamental energy losses of nickelocene obtained from: ^asolution infra-red spectroscopy [8] and ^bthis work.

modes indicates that at a coverage of one monolayer, the molecular axis of nickelocene is perpendicular to the Ag(100) surface. This is also suggested by the lack of intensity of the E_{1u} modes that would be dipole-active and therefore observable in the specular direction if the molecule adsorbed parallel to the surface or significantly canted from the surface normal.

These findings are contrary to the conclusions drawn in an earlier study of NiCp₂ on Ag(100) with angle-resolved photoemission spectroscopy [7] in which the molecular axis was found to be tilted with respect to the surface normal. However, the angular photoemission results were performed on approximately 40 L nickelocene exposed surfaces, which we estimate to be 3–5 monolayers thick. Figure 4 shows the electron-energy-loss spec-

trum for nickelocene adsorbed on Ag(100) as a function of increasing coverage. The spectra, which are given for the specular direction, agree well with the solution IR data [8] in loss energies and, again, indicate that nickelocene is molecularly adsorbed with little perturbation of its bonding structure. The two modes with E_{1u} symmetry can be seen to increase in intensity as the coverage is increased. This is especially apparent at 1500 L.

Figure 5 shows the high coverage spectrum (top) along with its off-specular spectrum for this coverage (bottom). The two intense A_{2u} modes are again seen at 44.5 and 96.9 meV. Unlike the single monolayer spectra, the two E_{1u} modes are now seen at 16.5 and 124.4 meV with intensities comparable with the A_{2u} modes. All four of the modes are dipole-active, as seen when compar-

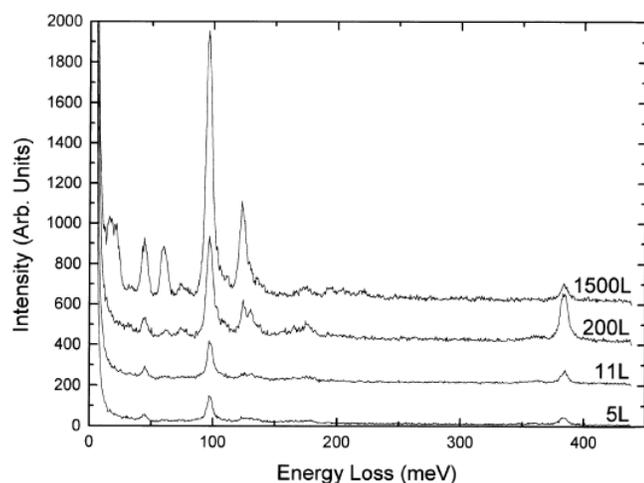


Figure 4. HREEL spectra with varying coverage of nickelocene on Ag(100), normalized with respect to the elastic peaks. The two modes with E_{1u} symmetry (16.5 and 124.4 meV) show a dramatic increase in intensity at high coverages.

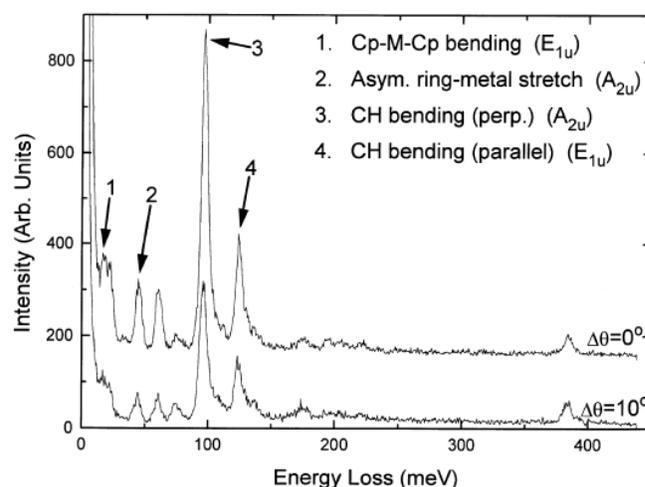


Figure 5. HREEL spectra for an exposure of 1500 Langmuir of nickelocene to Ag(100). Both A_{2u} and E_{1u} modes are dipole-active. Both spectra are shown on the same scale.

ing the on- and off-specular spectra, indicating that at this coverage, the dipolar motion associated with both sets of symmetries has a component perpendicular to the Ag(100) surface. Therefore, the molecular axis is not perpendicular to the surface at high coverages as seen in one monolayer of nickelocene. We postulate that this is caused by an increased disorder in the adsorbate layer as multilayers are formed, resulting in a randomized molecular orientation of the nickelocene with respect to the Ag(100) surface. We are currently investigating the cause of this change in orientation in more detail but speculate that it may be due to growth conditions being too rapid for well-ordered layers to form.

4. Conclusion

The high-resolution electron-energy-loss spectra show a good agreement with solution IR data [8], suggesting a molecularly adsorbed and weakly interacting system. The monolayer coverage data indicate that nickelocene adsorbs non-dissociatively with the molecular axis approximately perpendicular to the Ag(100) surface at 135 K. At very high coverages, the molecules become canted or randomized in orientation with respect to the surface normal, possibly due to rapid growth conditions for high coverages.

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