

## Bonding Configurations for Nickelocene on Ag(100) and Steric Effects in Thermal Desorption

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The molecular adsorption and desorption of nickelocene,  $\text{Ni}(\text{C}_5\text{H}_5)_2$ , on Ag(100) has been studied by coverage dependent angle-resolved thermal desorption. The angle-resolved thermal desorption of nickelocene is unusual in that the molecular orientation is seen to affect the angular dependence of molecular desorption. The coexistence of two chemisorption phases for molecular nickelocene adsorption on Ag(100) near the desorption temperature of approximately 230 K is identified. One phase, with the bonding configuration of the nickelocene molecular axis along the surface normal, dominates monolayer and submonolayer coverages. Another phase, with the molecular axis not along the surface normal, appears to dominate at higher coverages. The results are discussed in the context of rehybridization and recent angle-resolved photoemission and high-resolution electron energy loss measurements.

Nickelocene is one of the few adsorbates on a single crystal surface that has exhibited significantly enhanced desorption away from the surface normal.<sup>1</sup> This has been attributed to a combination of a “canted” bonding configuration of the molecular axis away from the Ag(100) surface normal and steric effects in the angle-resolved thermal desorption process.<sup>1</sup> Support for this postulate is seen in the far larger heat of desorption in the normal direction than off normal. The adsorption of nickelocene on Ag(100), at or below 150 K, has been shown to be molecular by angle-resolved photoemission,<sup>1</sup> high-resolution electron energy loss (HREELS),<sup>2</sup> and thermal desorption.<sup>1</sup> The heat of desorption was seen to be relatively weak at about  $\frac{1}{2}$  eV per molecule, though very dependent upon emission angle.

High-resolution electron energy loss spectroscopy (HREELS) finds that the bonding configuration for nickelocene at monolayer and submonolayer coverages on Ag(100) at 135 K places the molecular axis along the surface normal.<sup>2</sup> Apparently in contradiction to the HREELS data, the application of symmetry and selection rules to angle-resolved photoemission indicate that the bonding configuration must have the molecular axis canted away from the surface normal for 2 or more molecular layers of nickelocene.<sup>1</sup> With the bonding of nickelocene in the canted configuration, we now have a unique experimental example where steric effects cause the angle-resolved thermal desorption to deviate strongly from the expected  $\cos^\beta \theta$  distribution<sup>3</sup> (where  $\theta$  is the angle off normal and  $\beta$  is the critical exponent, which is seen experimentally to vary from 1 to 4.5).<sup>4</sup> We show, in this paper, this unusual behavior in thermal desorption, identified in a previous study for nickelocene,<sup>1</sup> depends on the desorption state as well as upon coverage.

The thermal desorption studies were undertaken in an ultrahigh vacuum chamber with sample cooling to 130 K. The measurements were taken with a quadrupole mass spectrometer

(Dycor) operated in the pulse counting mode and with the temperature measured by a calibrated chromel–alumel thermocouple, as has been described elsewhere.<sup>5,6</sup> The quadrupole mass spectrometer was differentially pumped by an ion pump and has an angular acceptance of less than  $\pm 3^\circ$  off the spectrometer axis. The surface was cleaned and characterized as described in detail elsewhere.<sup>1,5</sup>

There does exist evidence for different chemisorption states for molecular adsorption of nickelocene in the thermal desorption data. With increasing nickelocene coverages (increasing exposure to Ag(100)), the desorption of nickelocene becomes increasingly resolved into two features occurring at two different temperatures (following molecular adsorption at 130 K, as seen in the insert to Figure 1). Figure 2 shows that the occupation of the desorption feature at the higher temperature of about 230 K (peak B) increases with a lower rate than the coverage of the lower temperature thermal desorption feature (peak A) with increasing exposure. The lower temperature thermal desorption feature (peak A) desorbs at about 212 K and dominates the desorption spectrum at coverages higher than 6 langmuirs (1 langmuir =  $1 \times 10^{-6}$  Torr·s). This is an exposure about equivalent to the adsorption of a monolayer.<sup>1,2</sup> This has been summarized in Figure 2.

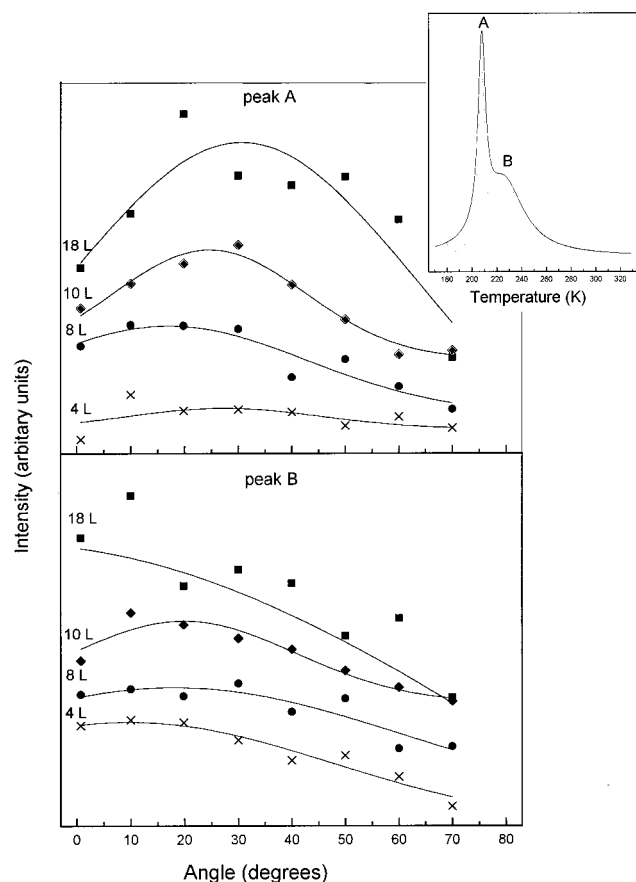
Definitive assignment of the origin of the states A and B is not possible with the results available, but the desorption characteristics differ substantially, not just in the desorption energetics, as indicated previously.<sup>1</sup> The emergence of peak A and relative suppression of peak B suggest that state A could be representative of adsorption beyond the first layer, which directly bonds with the Ag(100) substrate. This is consistent with the changes in relative sticking coefficient noted earlier (Figure 2). Ultimately, this is the possible origin for the HREELS evidence for an upright bonding configuration for nickelocene at low coverages and ARUPS derived canted bonding configuration at higher coverages.

Angle-resolved thermal desorption studies show that the desorption of nickelocene is fairly uniform in emission angle

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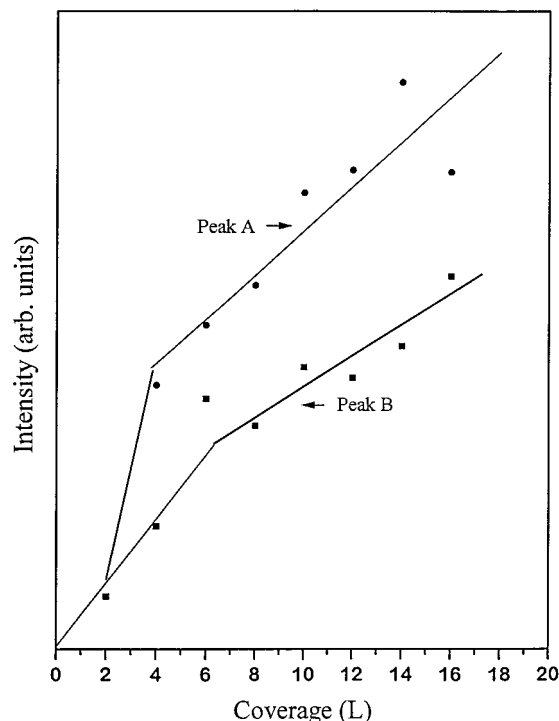
<sup>‡</sup> Salford University.



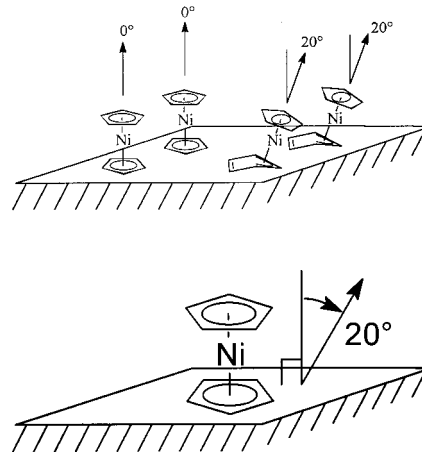
**Figure 1.** Integrated intensity of the thermal desorption features for each desorption state (states A and B, see text and the insert) as a function of emission angle. The data were acquired from thermal desorption spectra all taken for a heating rate of 3°/s following nickelocene adsorption on Ag(100) at 150 K. Four exposures are compared. The intensity data suggest that thermal desorption of molecular nickelocene occurs preferentially at more than 20–25° off normal at the higher coverages for desorption state A (see text) but not for state B. The scatter in the data and the lower signal in the thermal desorption spectra at lower coverages make such an assignment at the lower coverages very difficult. Deconvolution of the thermal desorption spectra of the molecular nickelocene components into two desorption peaks is shown in the inset.

following 4 and 8 langmuirs exposure for both desorption states A and B. At coverages corresponding to greater exposures, starting at about 10 langmuirs, desorption is peaked at an angle off normal (Figure 1), for the lower temperature desorption state (desorption state A). This is clearly not the expected cosine angular distribution, but unlike in previous work,<sup>1</sup> we can clearly see that this anomalous angular profile for desorption is restricted to only one of the two desorption states (i.e., to state A not B).

This angle-resolved thermal desorption eliminates some of the discrepancies between earlier HREELS data and angle-resolved photoemission. In the monolayer regime, the angle-resolved thermal desorption is dominated by desorption state B and the data and there is no strong off-normal desorption. This is consistent with the upright bonding configuration found in HREELS,<sup>2</sup> where the molecular axis is along the surface normal. Upon completion of a nickelocene monolayer (8 Langmuirs nickelocene exposure under our conditions), another nickelocene desorption state (desorption state A) is observed with strong angular thermal desorption anisotropy. We have postulated that a canted bonding orientation adopted by nickelocene on Ag(100) leads to lateral interactions and possible steric effects



**Figure 2.** Relative surface coverage of nickelocene as a function of exposure for each desorption state. The adsorption curves were estimated from the integral of the thermal desorption spectra following adsorption of nickelocene on Ag(100) at 130 K.



**Figure 3.** Possible bonding configurations of molecular nickelocene on Ag(100) at 150 K consistent with the angle-resolved photoemission results. The "interlocking" nature of the molecules at higher coverages and with the canted configuration is both geometrically possible and consistent with the observed angular dependence of molecular thermal desorption of nickelocene from Ag(100). We cannot specify the cant angle  $\theta$  on the basis of our data except to note that  $10^\circ \ll \theta \ll 40^\circ$ .

could dominate the desorption process.<sup>1</sup> These steric effects would occur only at the higher coverages from the evidence provided here and would hinder molecular desorption in the expected normal direction. The strong steric effects for this weaker chemisorption phase (state A) are consistent with the canted bonding configuration deduced from angle-resolved photoemission.<sup>1</sup>

This result is very unusual and not typical of most models of thermal desorption.<sup>3,4</sup> The origin of the canted configuration cannot be ascertained solely on the basis of this work. The angle-resolved thermal desorption data suggest that the nickelocene is oriented 20–25° off the normal (Figure 1). This angle is strongly reminiscent of  $(C_5H_5)_2W(CO)_2$  which contains a

trihaptocyclopentadienyl ligand bent along its 1,3-axis by  $20^\circ$ .<sup>7</sup> This is also a 20 electron complex, which by rehybridization changes from a 20 electron valence configuration to a more stable configuration about the central metal. For nickelocene on Ag(100), rehybridization, while at a cost of strain, may add stability to the 20 electron complex of nickelocene. Multiple and nonequilibrium molecular chemisorption states have been postulated for ferrocene adsorption on Ag(100)<sup>5</sup> but are clearly evident for molecular nickelocene adsorption on Ag(100) presented here.

Angle-resolved thermal desorption clearly shows different bonding properties for the two different desorption states. With the existence of these two states, the apparent contradiction between EELS and angle-resolved photoemission can be reconciled. The two different desorption states have different angular desorption characteristics and probably have different bonding configurations. These two possible bonding configurations of nickelocene, based upon this combination of the present angle-resolved thermal desorption results and previous HREELS data<sup>2</sup> and angle-resolved photoemission,<sup>1</sup> are schematically shown in Figure 3.

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