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### The Influence of Surface Atomic Steps on Site-Selective Adsorption Processes. Ethylidyne Formation on Rh{111} and Rh{331}

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Crystal defects such as steps and kinks are considered to be active sites which enhance molecular bond-breaking events in heterogeneous catalytic reactions.<sup>1</sup> In this communication, we present new evidence that suggests that for a class of site-specific reactions, these defects may actually inhibit the desired reaction pathway. Our conclusions are based on studies of CO and C<sub>2</sub>H<sub>4</sub> adsorption on Rh{111} and Rh{331} single crystal surfaces at room temperature. These model systems are of interest for several reasons. The Rh{111} surface as depicted at Figure 1a possesses an array of three-fold sites so as to accommodate the observed c(4 × 2) low energy electron diffraction (LEED)<sup>2</sup> structure for ethylidyne. The Rh{331} surface, however, is characterized by three rows of a {111} terrace and a {111} single atomic step as shown in Figure 1b. This structure contains only 80% of the number of three-fold sites that are present on Rh{111}. Ethylene undergoes dehydrogenation to CCH<sub>3</sub> (ethylidyne) and presumably

requires a three-fold symmetric anchoring position.<sup>3</sup> Carbon monoxide, on the other hand, has been observed to bond to a plethora of binding sites, the nature of which are coverage dependent.<sup>2,4,5</sup> By simultaneously dosing both surfaces with equal amounts of CO or C<sub>2</sub>H<sub>4</sub>, we show with use of X-ray photoelectron spectroscopy (XPS) that the coverage of CO on the two crystal surfaces is identical, while the ethylidyne coverage on Rh{331} scales precisely with the number of available active sites. The results suggest that these step defects may then inhibit certain structure-sensitive reactions and that ethylidyne itself may be a novel titrant to determine the number of these sites on polycrystalline surfaces.<sup>6</sup>

Experiments were performed with use of a multitechnique surface analysis system described earlier.<sup>7</sup> Both the {111} and {331} crystals were affixed to the same sample manipulator and cleaned by using previously developed procedures until no impurity peaks could be observed by XPS. The crystals were then annealed at 1300 K until the characteristic LEED diffraction pattern was observed at room temperature and were subsequently dosed at 300 K with 10 langmuirs<sup>6</sup> of Matheson Research grade CO or C<sub>2</sub>H<sub>4</sub> (at 10<sup>-7</sup> Torr for 100 s). The C 1s and O 1s peak areas were determined by subtracting the background Rh signal. The pho-

(1) Davis, S. M.; Zaera, F.; Somorjai, G. A. *J. Am. Chem. Soc.* **1982**, *104*, 7453.

(2) Castner, D. G.; Sexton, B. A.; Somorjai, G. A. *Surf. Sci.* **1978**, *71*, 519.

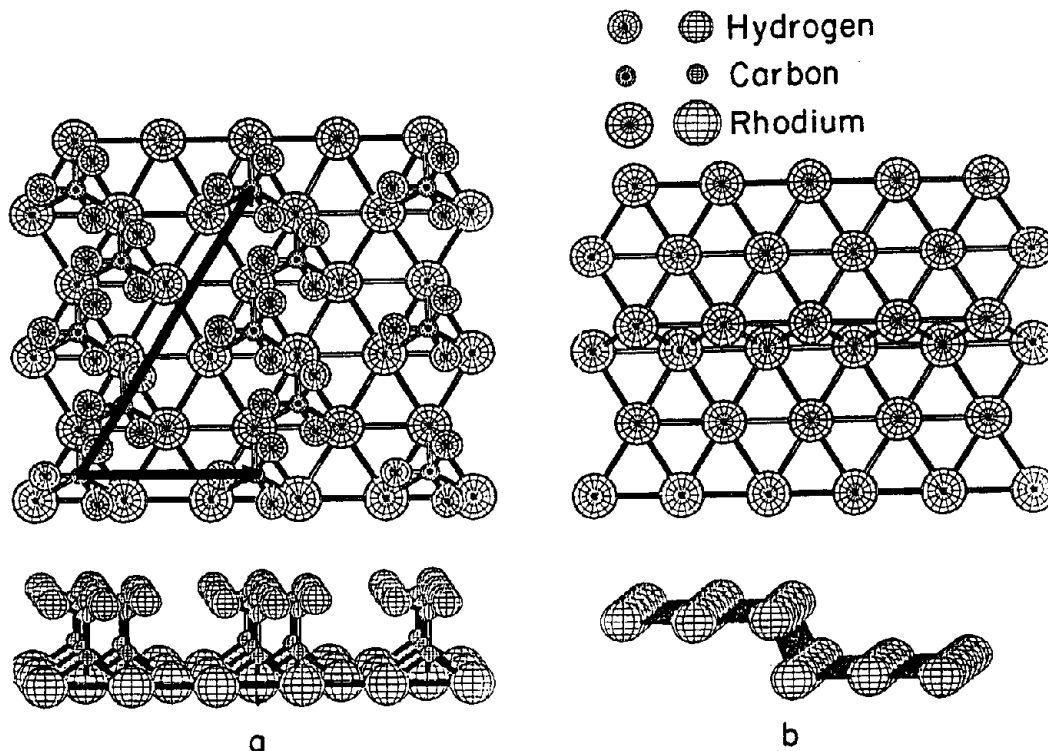
(3) Skinner, P.; Howard, M. L.; Oxtun, I. A.; Kettle, S. F. A.; Powell, D. B.; Sheppard, N. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1203.

(4) Dubois, L. H.; Somorjai, G. A. *Surf. Sci.* **1980**, *91*, 514.

(5) DeLouise, L. A.; White, E. J.; Winograd, N. *Surf. Sci.* **1984**, *147*, 252.

(6) Beebe, T. P.; Yates, J. T. *Surf. Sci.* **1986**, *173*, L606.

(7) DeLouise, L. A.; Winograd, N. *Surf. Sci.* **1984**, *138*, 417.



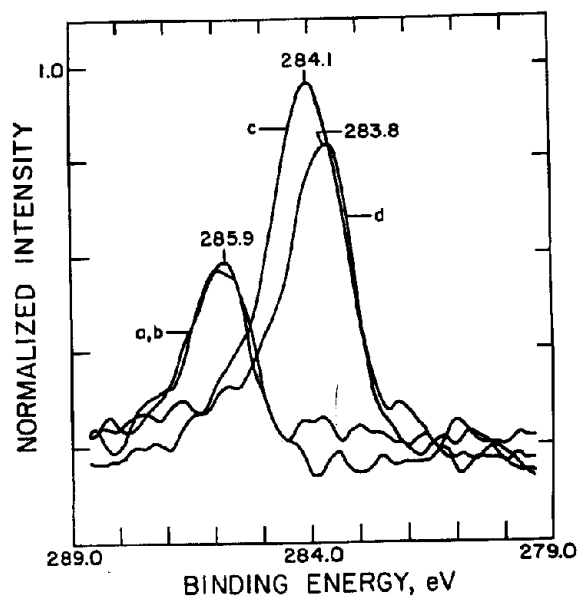
**Figure 1.** Schematic diagram of Rh[111] and Rh[331]. The Rh[111] surface with alternating rows of ethylidyne is shown in (a). The  $c(4 \times 2)$  real space lattice vectors are shown. Note: The van der Waals radii for C and Rh are reduced for clarity. The Rh[331] surface with the three-row {111} terrace and the {111} step is illustrated in (b).

toelectron take-off angle was kept at  $35^\circ$  as measured from the plane of the surface to avoid focusing effects. In addition, the acceptance aperture was widened to integrate possible angular anisotropies in the electron yield. All XPS binding energies (BE's) are reported with respect to the Rh Fermi energy which places the Rh  $3d_{5/2}$  peak at 307.1 eV.

Reproducibility of XPS peak area measurements was established by examining CO chemisorption on the two crystal surfaces and to provide a C coverage reference for the ethylidyne studies. As shown in Figure 2a,b both surfaces yield similar XPS spectra exhibiting a C 1s BE of 285.9 eV. Previous XPS studies of the O 1s line shape suggest that similar amounts of linear and bridge sites are observed on both surfaces under these conditions.<sup>5</sup> The saturation coverage is therefore determined more by interactions between CO molecules than by the number of available surface bonding sites.

After exposure of the clean surfaces to 10 L of ethylene at room temperature, a dramatically different picture emerges from analysis of the XPS spectra. Under similar conditions, both electron energy loss spectroscopy (EELS)<sup>8</sup> and LEED<sup>9</sup> experiments on Rh[111] suggest the dominant surface species is ethylidyne. The XPS C 1s BE of 284.1 eV is certainly consistent with this assignment, although we could not rule out the possibility of carbide formation as its C 1s BE appears at 283.8 eV.<sup>10</sup> Thermal stability experiments performed by recording XPS spectra between 298 and 800 K suggest there is a similar reaction pathway for ethylene adsorption on Rh[331].<sup>11</sup>

There are two crucial pieces of information contained in the C 1s intensity measurements given in Figure 2. First, for Rh[111], the integrated peak area shows that the  $c(4 \times 2)$  overlayer structure exhibits a coverage of 94% of that found for CO after correcting for the fact that ethylidyne contains 2 C atoms. The CO coverage has been determined to be 0.62 monolayer (ML)



**Figure 2.** Carbon 1s photoelectron spectra for (a,b) a 10-L exposure of CO on the Rh[111] and Rh[331] surfaces at 300 K, (c) a 10-L exposure of  $C_2H_4$  on the Rh[111] surface at 300 K, and (d) a 10-L exposure of  $C_2H_4$  on the Rh[331] surface at 300 K. The Rh  $3d_{5/2}$  peak areas are equivalent to within 97% of each other for the two crystal faces.<sup>10</sup>

from LEED, EELS, and thermal desorption experiments<sup>2,12</sup> implying that the ethylidyne coverage is 0.58 ML. The conventional  $c(4 \times 2)$  LEED structure implies a coverage of 0.25 ML. Note that an anomalously high carbon coverage has been previously reported on Pt[111].<sup>13</sup> Shown in Figure 1 is our proposed structure which would also yield a  $c(4 \times 2)$  pattern. This unique alternating row configuration, with sterically locked hydrogen atoms, corresponds to 0.5 ML coverage and appears to be a highly stabilized geometry. The second important feature is that the C is integrated

(8) Dubois, L. H.; Castner, D. G.; Somorjai, G. A. *J. Chem. Phys.* **1980**, *72*(9) 5234.

(9) Koestner, R. J.; Van Hove, M. A.; Somorjai, G. A. *Surf. Sci.* **1982**, *121*, 321.

(10) Levis, R. J.; Winograd, N., in preparation.

(11) Levis, R. J.; DeLouise, L. A.; White, E. J.; Winograd, N., in preparation.

(12) Dubois, L. H.; Somaridi, G. A. *Surf. Sci.* **1980**, *91*, S14.

(13) Yo, R.; Gusafsson, T. *Surf. Sci.* **1987**, *182*, L234. Freyer, N.; Pirug, G.; Bonzel, H. P. *Surf. Sci.* **1983**, *125*, 327.

intensity for Rh{331} is reduced to  $79 \pm 2\%$  of that found for Rh{111}. The LEED I-V<sup>9</sup> calculations and EELS<sup>8</sup> measurements suggest that ethylidyne binds to three-fold sites on the {111} plane. The observed decrease in C 1s intensity on Rh{331} scales precisely as the decrease in the number of three-fold holes available for binding. Note from Figure 2 that the presence of the step removes 20%<sup>14</sup> of these sites. Although it is not yet possible to identify the overlayer structure on Rh{331}, we note that it is possible to construct the same zig-zag geometry postulated for Rh{111} without steric interference from the step itself.

In summary, we have performed accurate carbon coverage measurements for CO and C<sub>2</sub>H<sub>4</sub> adsorption on Rh{111} and Rh{331}. The results suggest that a very stable structure with interlocking hydrogen atoms is formed on the {111} plane and that the presence of the step on the {331} surface inhibits ethylidyne formation by reducing the number of active sites. It is of interest that the high site specificity of this reaction may provide a selective titrant for threefold sites on polycrystalline surfaces.

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(14) The surface atom density ratio for Rh{331}/Rh{111} is 1.2, including step atoms (or step sites). Removing the step atoms (or step sites), covering  $\frac{1}{3}$  of the Rh{331} surface leaves a ratio of 0.80 or 80%.