Molecule-Induced Displacive Reconstruction in a Substrate Surface: Ethylidyne Adsorbed on Rh(111) Studied by Low-Energy-Electron Diffraction

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It is found for the first time that a molecule can induce a displacive reconstruction in the substrate on which it is adsorbed. This is observed in a refined structure determination of Rh(111)(2×2)-C$_2$H$_3$, in which C$_2$H$_3$ (ethylidyne) is adsorbed on the Rh(111) single-crystal surface. This result strengthens an earlier hypothesis that catalytic reactions are usually accompanied by distortions in the catalyst, which can profoundly affect reaction rates and selectivities.

Adsorbates are known to induce surface restructuring: The substrate structure is either strongly modified (we call this "bond-breaking reconstruction") or else weakly distorted (also called "displacive reconstruction" or relaxation) [1-3]. Bond-breaking reconstruction is seen, for instance, with alkali adsorption on Ni [4], Cu [5], Pd [6], Ag [7], and Au(110) [8]. Examples of displacive reconstruction include the adsorption of C [9], N [10], O [11], and S [12] on Ni(100). Detailed structures have been determined for most of these cases of atomic adsorption. However, no adsorbate-induced restructuring has yet been observed for molecular adsorption, due to the complexity of the analysis. This case is particularly important in that the traditional catalytic picture of the substrate passively affecting the adsorbed molecule should be modified: The molecule can also strongly affect the catalyst and therefore its properties [13]. Substrate restructuring is already known to considerably affect the mechanism of atomic surface diffusion [14-17].

We report the first observation of molecule-induced relaxations: It includes both bucklings and lateral relaxations in the substrate layers. It was found for ethylidyne (C$_2$H$_3$), produced by adsorption of acetylene or ethylene on Rh(111). This structure was investigated previously [18] by a conventional LEED intensity analysis [19]: It was then, however, assumed that no relaxations occur in the substrate. We have now reexamined the same database by applying the recent automated tensor LEED method [20]. This powerful approach is particularly effective in analyzing adsorbate-induced relaxations.

To perform the structural determination, we applied our recently developed automated tensor LEED method [20], which permits the efficient automatic fitting of many independent structural parameters. It involves first making a full dynamical LEED calculation for a reference structure, for which we selected our best guess, namely, the earlier structural result [18]: a C-C axis perpendicular to the surface, centered over an hcp-type threefold hollow site. Using tensor LEED, distorted structures around that reference structure were examined: We allowed all atomic coordinates to vary in the top two metal layers and in the molecular layer (H atoms are totally ignored). With a minimization algorithm for the Pendry R factor, the fitting was accomplished automatically for the resulting thirty adjustable structural coordinates (the muffin-tin zero is also fitted at the same time). The analysis was performed independently for two measured data sets at different angles of incidence to test the consistency of the results.

The LEED experiment was described previously [18]. In the new analysis we used two sets of intensity versus electron energy curves, at the polar incidence angles of 0° and 31°; these comprise eight and eleven symmetrically independent beams with cumulative energy ranges of 732 and 1008 eV, respectively. Since off-normal polar angles are less well determined than at normal incidence, we checked the 31° angle explicitly with full structural analyses at nearby angles, and only found structural variations within our error bars for 1° changes of the polar angle [21].

Our resulting structure is shown in Fig. 1, averaged over the two data sets. The fitted atomic coordinates from the two data sets agree within 0.02 Å. The level of agreement between mutually symmetrical coordinates is 0.02-0.05 Å, if we assume that the structure has, in fact, threefold rotational symmetry and mirror planes (this symmetry is not guaranteed, but the results strongly suggest it). Figure 1 and our further discussion assume this symmetry, obtained by symmetrically averaging the independently fitted coordinates. The best new Pendry R-factor value is 0.32 for the normal-incidence data, compared to 0.45 assuming a rigid substrate (a similar reduction holds for the off-normal-incidence data).

The C-C axis of ethylidyne is confirmed to be perpendicular to the surface within our accuracy, i.e., within 2.5°. The C-C bond length is found to be 1.48 ± 0.04 Å, compared to 1.45 ± 0.10 Å assuming a rigid substrate [18].

The lower carbon atom of ethylidyne has three Rh neighbors in the top metal layer: There is a tendency for these atoms to be pushed radially outwards from the C-C axis by 0.05 ± 0.05 Å from their bulk positions (there is
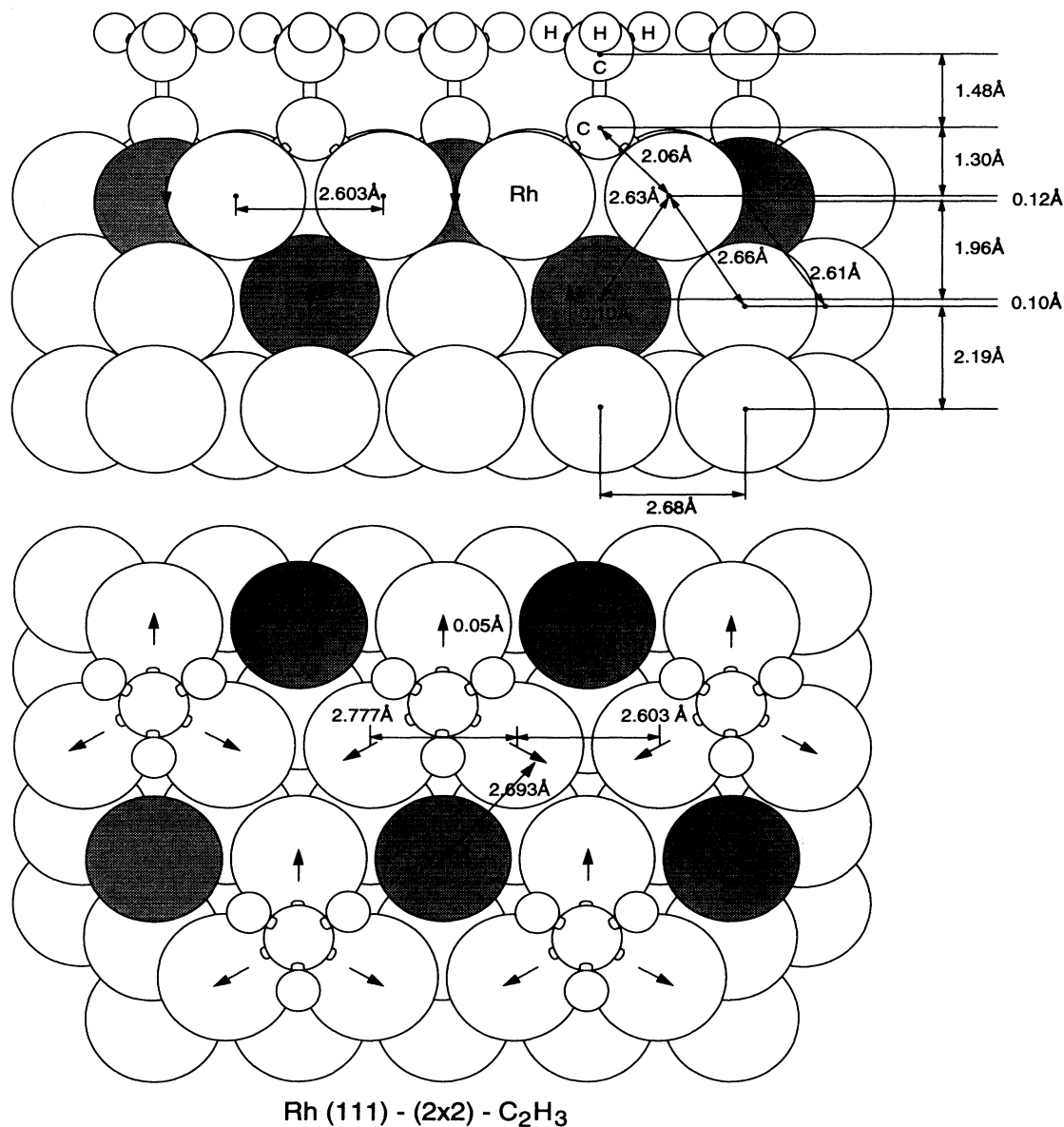
Rh (111) - (2x2) - C₂H₃

FIG. 1. Side view (top panel) and top view (lower panel) of Rh(111)(2×2)-C₂H₃ (ethylidyne, with guessed H positions). Gray atoms have relaxed perpendicular to the surface from bulk positions. Substrate relaxations are drawn to scale, emphasized by arrows and labeled by their magnitudes.

no sign of a rotation of this triplet of Rh atoms about the ethylidyne axis, within 0.10 Å). The corresponding C-Rh layer spacing is 1.30 ± 0.04 Å, giving C-Rh bond lengths of 2.06 ± 0.10 Å, while the C-C-Rh bond angles are $129° \pm 2°$ (the corresponding values of the earlier analysis [18] were 1.31 ± 0.10 Å, 2.03 ± 0.07 Å, and $130° \pm 2.5°$, respectively). The fourth Rh atom of the (2×2) unit cell in the top metal layer (this atom is not bonded to the ethylidyne and is drawn gray in Fig. 1) sinks into the surface by 0.12 ± 0.04 Å, resulting in a buckled layer.

The hcp hollow site of the ethylidyne includes a Rh atom directly below it in the second metal layer: This atom (also drawn gray in Fig. 1) is pulled up towards the ethylidyne by 0.10 ± 0.05 Å, relative to the three other Rh atoms of the (2×2) unit cell in the second metal layer (these three have no detectable lateral or perpendicular relaxations from their bulk positions). Consequently, the spacing between mutually closely bonded Rh atoms (below the ethylidyne) in the first and second metal layers is 2.08 ± 0.05 Å, and 2.06 ± 0.05 Å away from the ethylidyne. These spacings correspond to bond lengths of

2.63 ± 0.03 and 2.61 ± 0.03 Å, respectively, while other Rh-Rh bond lengths between first and second layers are 2.66 ± 0.03 Å. For comparison, the bulk interlayer spacing is 2.19 Å and the bulk Rh-Rh bond length is 2.68 Å. The relaxations in the top two metal layers can be regarded as the outward lifting (and slight spreading out) of the three first-layer and one second-layer Rh atoms directly below the ethylidyne, while leaving the other Rh atoms in those layers largely unchanged.

The formation of strong adsorbate-metal bonds provides the thermodynamic driving force for the restructuring of the substrate, which may also be accompanied by the weakening of bonds within the substrate. The ethylidyne-induced relaxation of Rh(111) is most likely an example of a general phenomenon of molecule-induced restructuring of substrates. Less close-packed metal substrates are likely to restructure even more readily than the close-packed (111) fcc crystal face.

These results point to the complexity of the surface structures that may be produced when surface chemical bonds are formed. We should therefore explore the structural transformations that occur on both sides of the adsorption bond, on the substrate side as well as on the molecular side. As a result, there may be significant effects on many surface-sensitive phenomena, including catalysis, adhesion, and friction, as well as electronic, optical, and magnetic properties.

Molecule-induced substrate restructuring will also alter the coverage-dependent adsorbate-adsorbate interactions and other coadsorption phenomena. It would be of great interest to perform total-energy calculations to investigate adsorbate-induced relaxations for atoms as well as molecules. Their role in surface reactions should also be studied, including, in particular, the effect on the electronic structure.

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[21] The structural error bars are chosen to correspond to a 20% change in R-factor value from its minimum. This 20% figure is our empirical observation of error bars quoted in many reported surface structure results. However, some guesswork is involved since our automated tensor LEED does not provide the complete R-factor profile in all dimensions near the minimum. In addition, error bars for different structural parameters should strictly be correlated through a curvature matrix [see J. N. Andersen, H. B. Nielsen, L. Petersen, and D. L. Adams, J. Phys. C 17, 173 (1984)].