Communications to the Editor

Distinctive Reactivities of Surface-Bound H and Bulk H for the Catalytic Hydrogenation of Acetylene

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Received June 5, 1998

We report that both surface-bound H atoms and bulk H atoms, upon moving out from the bulk of a Ni single crystal to its surface of a (111) orientation, are reactive with adsorbed C_2H_2, but the two kinds of H atoms have unique product distributions. Both bulk H and surface-bound H react with C_2H_2 to produce adsorbed ethylidyne, CCH_3, while only bulk H hydrogenates C_2H_2 to gas-phase ethylene and ethane, the products of interest in acetylene hydrogenation catalysis for the purification of ethylene streams.[1] Their distinct reactivities arise from both their different directions of approach to the π orbitals of the unsaturated hydrocarbon[2] and their substantially different energetics. These observations demonstrate that H embedded in the metal catalyst is a reactant in alkyne hydrogenation and is not solely a source of surface-bound H which then reacts with acetylene, as proposed from correlations between the hydrogenation activity of Raney Ni[3−6] and Pd catalysts[1,7−9] and the amount of H absorbed in these catalysts. The reactivities of these two kinds of H atoms are clearly distinguished in this experiment because of the capability to synthesize either bulk H or surface-bound H cleanly in an ultrahigh vacuum environment.

Hydrogen is embedded into Ni at 120 K by exposure to a H atom beam.[10] The surface-bound H resulting from this procedure is removed by recombinative desorption induced by the impacts of 144 kcal/mol Xe atoms.[11,12] Acetylene is then adsorbed by exposure to a C_2H_2 beam. High-resolution electron energy loss (HREEL) spectroscopy verifies the efficacy of the Xe beam in sweeping the surface clean of H, confirms the presence of both adsorbed C_2H_2 and bulk H, shows that the C−C bond lies parallel to the surface, and demonstrates that the presence of bulk H does not modify the C_2H_2−Ni interaction.[13−15] With the reactants synthesized, the crystal is heated at a rate of 2 K/s while a quadrupole mass spectrometer monitors the partial pressure at masses 2, 26, 27, and 30. Some of these thermal desorption spectra are shown in Figure 1a. The recombination and desorption of hydrogen occurring between 170 and 250 K arises from hydrogen emerging from the bulk, while the remaining hydrogen desorbs from the surface between 300 and 450 K.[10] At 180 K, the temperature at which bulk H emerges onto the surface, ethylene and ethane are observed to desorb rapidly. In addition, the adsorbed C_2H_2 reacts with the emerging bulk H to form adsorbed CCH_3, as a HREEL spectrum in Figure 2a, measured after heating the surface to 220 K, shows. The features at 457, 1025, 1129, 1336, 1410, 2883, and 2940 cm^{-1} are the Ni−C antisymmetric stretch, CH_3 rock, C−C stretch, CH_3 symmetric and antisymmetric deformation, and the C−H symmetric and antisymmetric stretch modes, respectively.[16] The feature at 950 cm^{-1} is the antisymmetric Ni−H mode.[10,16] The features at 690 and 860 cm^{-1} are the symmetric and antisymmetric C−H bending modes of C_2H_2, respectively.[14,16]

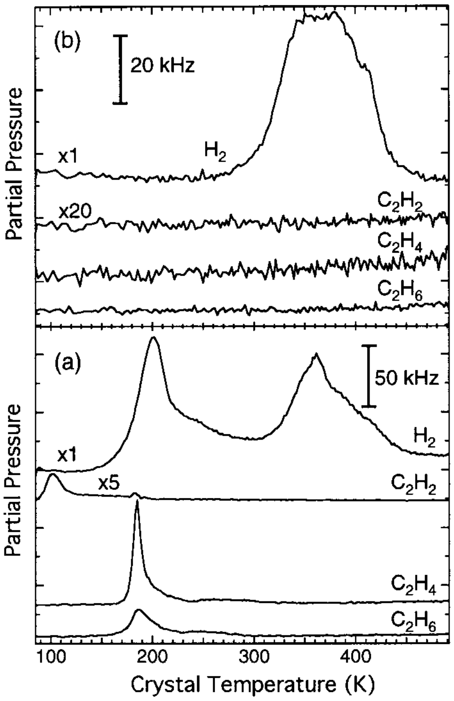

Figure 1. (a) Thermal desorption spectra from 0.25 ML of C_2H_2 adsorbed on Ni(111) with an equivalent of 1.8 ML of H embedded in the Ni bulk. Partial pressures are corrected for ^{13}C contribution and for ethane and ethylene cracking patterns at 70 eV electron energy. C_2H_2 feature at 100 K arises from desorption from the surrounding cryostat. (b) Thermal desorption spectra from a coadsorbed layer of 0.13 ML of C_2H_2 and 0.7 ML of surface-bound H.

The unreactivity of surface-bound H with C_2H_2 to form gas-phase hydrogenation products is demonstrated as follows. A coadsorbed layer of 0.17 ML of C_2H_2 and 0.5 ML of H is formed at the center of the crystal at 80 K, and its EEL spectrum is shown in Figure 2b. Comparison of this spectrum with that of C_2H_2 in Figure 2c shows that the relative intensities, but not the frequen-

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S0002-7863(98)01961-1 CCC: $15.00

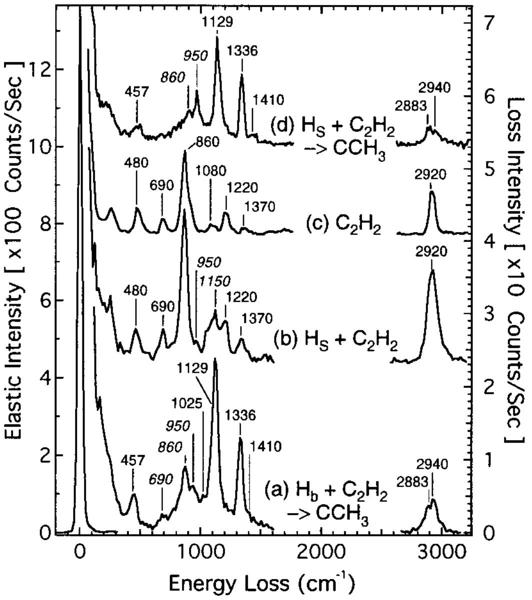

Figure 2. (a) EEL spectrum predominantly of CCH_3 at 80 K, formed by the reaction, at 180−200 K, of 0.22 ML of C_2H_2 with an equivalent of 4.2 ML of H embedded in bulk Ni. Recorded 5° from the specular angle with $E_i = 6.5$ eV, $\Delta E_{fwhm} = 40$ cm^{-1}, channel width = 12 cm^{-1}, and signal integration time per channel = 41 s. Frequency labels in *italics* mark features not associated with CCH_3. (b) EEL spectrum of 0.17 ML of C_2H_2 coadsorbed with 0.5 ML of H at 80 K. Recorded 10° from the specular angle with $E_i = 6.5$ eV, $\Delta E_{fwhm} = 44$ cm^{-1}, channel width = 16 cm^{-1}, and signal integration time per channel = 24 s. Frequency labels in *italics* mark features not associated with C_2H_2. (c) EEL spectrum of 0.25 ML of C_2H_2 at 80 K. Recorded 8° from specular angle with $E_i = 6.5$ eV, $\Delta E_{fwhm} = 39$ cm^{-1}, channel width = 16 cm^{-1}, and signal integration time per channel = 56 s. Relative intensities of the features do not vary between 0.17 and 0.25 ML of C_2H_2 or between 8° and 10° detection angle. (d) EEL spectrum predominantly of CCH_3 at 80 K, formed by reaction of surface bound H with 0.17 ML of C_2H_2 at 270 K. Recorded 10° from the specular angle with $E_i = 6.5$ eV, $\Delta E_{fwhm} = 44$ cm^{-1}, channel width = 16 cm^{-1}, and signal integration time per channel = 34 s. Frequency labels in *italics* mark features not associated with CCH_3.

cies, of the C_2H_2 loss features have been affected by the coadsorbed H. The crystal is then heated, but as Figure 1b shows, no ethylene or ethane are observed to desorb under these conditions or for any ratio of surface H to C_2H_2 that was investigated in the range of 15 to 2. Furthermore, measurements of the C Auger intensity confirm that no C has been removed from the surface. Rather, the surface-bound H has reacted with the C_2H_2 to form adsorbed CCH_3, as shown by the HREEL spectrum in Figure 2d. This spectrum was measured after three sequences of exposure of the same 0.17 ML of C_2H_2 to 12 000 L of H_2 at 270 K followed by a 25 min anneal at 270 K, to maximize the production of CCH_3. The rate of CCH_3 production below 260 K is too slow for any CCH_3 to be detected. Above 280 K, the desorption of H_2 leads to the dissociation of CCH_3 to form C_2H_2.

The observed reactivity of both bulk H and surface-bound H atoms with adsorbed C_2H_2 is in stark contrast to the unreactivity of surface-bound H and the singular reactivity of bulk H with ethylene, but is consistent with and constitutes strong evidence for the direction of the approach of the H atom to the π orbitals of the unsaturated hydrocarbon as a critical element in the catalytic hydrogenation activity.[2] Like ethylene, C_2H_2 has rehybridized π orbitals directed toward the metal which are available for bonding and are accessible to the bulk H atoms as they approach the hydrocarbon from below upon emerging from the bulk. The accessibility of bulk H to these π orbitals results in hydrogenation of both hydrocarbons to gas-phase products. Unlike ethylene, C_2H_2 has a second rehybridized π orbital which lies approximately parallel to the surface. This π orbital is accessible to surface-bound H atoms, which have a roughly coplanar approach to the hydrocarbon and therefore react with C_2H_2. The inability of surface bound H atoms, with their side-on approach, to access the single π orbital on ethylene that is oriented toward the metal results in a barrier that is too large for ethylene hydrogenation by surface-bound H to proceed under these conditions.

The addition of either the first bulk H atom or the first surface-bound H atom to C_2H_2 results in a vinyl species, H_2CCH, which we believe to be the critical intermediate for CCH_3 formation. Although H_2CCH has not yet been identified spectroscopically in either reaction, presumably because of its short lifetime, its role is strongly suggested by the absence of CCH_3 production in the reaction of bulk H with C_2H_4.[2,13] Because hydrogen abstraction from C_2H_4 by a bulk H atom to form H_2CCH is endothermic, no H_2CCH and, therefore, no CCH_3 can be produced. In contrast, hydrogen abstraction from C_2H_4 by a gas-phase H atom to form H_2CCH is exothermic, and indeed, exposure of adsorbed C_2H_4 to H atoms readily results in adsorbed CCH_3.[13,16]

Recall that the reactions of both surface-bound H and bulk H with C_2H_2 produce CCH_3, while only the reaction of bulk H with C_2H_2 produces gas-phase C_2H_4. Although the mechanism for conversion of H_2CCH to CCH_3 is uncertain,[13] it is clear that a second H atom must be added to H_2CCH to form C_2H_4. Apparently, the rate of addition of a bulk H atom to H_2CCH to form gas-phase C_2H_4 competes favorably with conversion of H_2CCH to CCH_3 while the rate of addition of a surface-bound H atom to H_2CCH to form gas-phase C_2H_4 is too slow to compete effectively against conversion of H_2CCH to CCH_3. The faster rate for addition of bulk H may arise from its higher energy. A bulk H atom reacts with an adsorbate while it is a transiently energetic species emerging out of the bulk. It may be as much as 24 kcal/mol more energetic than a reacting surface-bound H atom,[10−12] whose energy is characterized by a thermal distribution at 270 K.

These results clearly demonstrate that the reactivities of surface-bound and bulk H atoms and their product distributions are distinct. Their distinctiveness arises from both their different directions of approach to the adsorbate and their large difference in energy. In a sense, the bulk H atom is a new kind of surface reactant with a chemistry of its own.

Acknowledgment. This work is supported by DoE (DE-FG02-89ER14035). We thank M. Gostein for a critical reading of this manuscript.

JA9819615