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Ethylene Hydrogenation on Ni(111) by Bulk Hydrogen

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We report that bulk H atoms, upon moving out from the bulk metal to the surface, readily hydrogenate C_2H_4 adsorbed on Ni(111) to form C_2H_6, while surface-bound H atoms have no hydrogenation activity under the conditions of these experiments. This result is the first observation of the role of bulk H specifically as a reactant in the hydrogenation of an unsaturated hydrocarbon on a transition metal and calls into question the generality of the Horiuti–Polanyi mechanism for catalytic hydrogenation reactions.[1] This result is also a plausible molecular level basis for the correlation between the hydrogenation activity of a Raney Ni catalyst and the H content in the catalyst.[2-5]

Kinetic limitations preclude the formation of H embedded in Ni under the low H_2 pressures attainable with routine ultrahigh-vacuum (UHV) surface techniques. We overcome these limitations with one of our recently developed methods for synthesizing bulk H under UHV conditions.[6,7] A beam of atomic H directed at a Ni single crystal held at 130 K yields up to an equivalent of 10 ML (monolayers) of H absorbed in the bulk metal but also leaves a monolayer of H bound to the surface. Since we wish to test first the reactivity of the bulk H, the surface-bound H must be removed. The removal is effected by collision-induced recombinative desorption whereby a 144 kcal/mol Xe beam with a 40° incident angle is directed at the surface. The impact of the Xe collision momentarily jostles the lattice, causing the adsorbed H to recombine and desorb while leaving the bulk H unperturbed.[8] The crystal at 80 K is then exposed to a beam of C_2H_4 to form an adsorbed layer at the center of the crystal whose coverage is varied from 0.01 ML to the 0.25-ML saturated, ordered overlayer. 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_4 and bulk H, shows that the C–C bond lies parallel to the surface, and indicates that the C atom hybridization is between sp^2 and sp^3. The identicalness of the ethylene vibrational spectrum to that of C_2H_4 adsorbed on Ni(111) without bulk H[9-11] demonstrates that the bulk H does not modify the C_2H_4–Ni interaction.

With the reactants now 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, 28, 29, 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 is known from our previous work[6,7] to arise from hydrogen emerging from the bulk whereas the remainder of the hydrogen is desorbing from the surface. At 180 K, the temperature at which the bulk H makes its way onto the surface, ethane is observed to desorb rapidly. The emergence of the bulk H onto the surface also causes rapid desorption of C_2H_4. Up to 65% of the C_2H_4 is hydrogenated to ethane under these conditions. No carbon-containing species remain on the surface above 220 K.

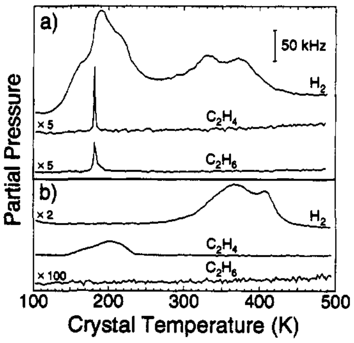

Figure 1. (a) Thermal desorption spectra from 0.025 ML of C_2H_4 adsorbed on Ni(111) with an equivalent of 2 ML of H embedded in the bulk metal. Partial pressures are corrected for ^{13}C contribution and for the ethane and ethylene cracking patterns at 70 eV electron energy. (b) Thermal desorption spectra from a coadsorbed layer of 0.25 ML of C_2H_4 and 0.26 ML of surface-bound H.

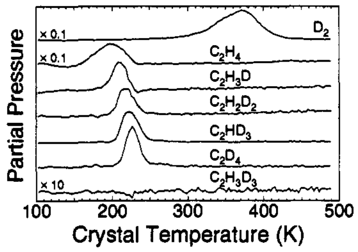

Figure 2. Thermal desorption spectra from a coadsorbed layer of 0.25 ML of C_2H_4 and 0.26 ML of surface-bound D. Same corrections as in Figure 1.

The hydrogenation activity of bulk H is now compared to that of surface-bound H. Coadsorbed layers of C_2H_4 and surface-bound H ranging between 0.05 and 0.25 ML and 0.57 and 0.26 ML coverage, respectively, are formed by exposing the crystal at 80 K to C_2H_4 and then to 5400 L of H_2. HREEL spectra show that the vibrational structure of C_2H_4 is unaffected by surface-bound H. The crystal temperature is then ramped, but no ethane is detected for any coverage condition, as shown in Figure 1b. Our sensitivity limit for ethane detection corresponds to the hydrogenation of 0.001 ML of adsorbed C_2H_4.

However, the surface-bound H experiment is intriguing because although surface-bound H does not hydrogenate C_2H_4, it is very reactive toward exchange with ethylene! A coadsorbed layer of 0.25 ML of C_2H_4 and 0.26 ML of surface-bound D is formed. The resulting thermal desorption spectra are shown in Figure 2. It is clear from the data that all the deuterated ethylenes, from C_2H_3D to C_2D_4, are produced. Since C_2H_4 slowly decomposes to adsorbed C_2H_2 in this temperature range,[12] it is likely that exchange is occurring in an equilibrium step between C_2H_4 and C_2H_3. The observation of exchange is a very important one because it demonstrates that it is not the accessibility of the surface-bound H to C_2H_4 that is precluding hydrogenation. Obviously, the surface-bound H (or D) is sufficiently mobile to approach C_2H_4 and to interact very strongly with it, even to exchange with it. Rather, the unreactivity of the surface H toward hydrogenation implies that the barrier to hydrogenation via a side-on approach to the lying down C_2H_4 molecule is just too high for the reaction to proceed under these conditions. However, if

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the H atom approaches C_2H_4 from underneath, which is the direction in which the rehybridized π orbitals are oriented, the barrier to hydrogenation is lower, and therefore the reaction proceeds readily. Indeed, the reaction coordinate for addition of a H atom to C_2H_4 in the gas phase involves a perpendicular approach to the plane of C_2H_4.[13]

To determine whether the direction of approach of the H atom is the sole requirement for hydrogenation, 0.01 ML of C_2H_4 is adsorbed on top of a surface-bound H monolayer, formed by heating a crystal containing bulk H to just above the temperature for desorption of bulk H. After verification of this adsorption geometry by HREELS, the crystal temperature is ramped at 2 K/s. No ethane is detected. Additional experiments carried out with C_2H_4 adsorbed on top of lower coverage H layers where the ethylene has varying degrees of interaction with the surface also result in no hydrogenation. This reactivity difference between the bulk and surface H atoms, despite their identical perpendicular direction of approach, likely results from the different energies of the two atoms. Bulk H atoms are propelled out of the bulk with roughly 13 kcal/mol of energy gained from descending the bulk/surface barrier[6,14] whereas surface H atoms possess a thermal energy distribution characterized by the crystal temperature. The difference in reactivity may also arise from different barriers to hydrogenation for the two cases. In the bulk H experiment, C_2H_4 is rehybridized by its strong interaction with Ni whereas C_2H_4 adsorbed on top of the surface H layer retains its gas-phase structure. Experiments are underway to delineate these possible origins for the reactivity difference.

It should be noted that if H_2 and then C_2H_4 are allowed to adsorb on the edges of the crystal, we do observe a small but detectable amount of hydrogenation. This hydrogenation activity from the crystal edges may arise from hydrogenation via bulk H whose production is facilitated by the rough surfaces of the crystal edges or may result from surface-bound H reacting with ethylene that has a very different structure on the crystal edges than on Ni(111). Either possibility may explain the small amount of C_2H_4 hydrogenation observed on Ni(100).[15] Our present results are consistent with a recent observation of ethylene hydrogenation on Ni(110)[16] where the hydrogenation occurs only with the hydrogen that has been interpreted as forming a Ni hydride.[17]

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