Low-Temperature Hydrogenation of Cyclohexene by Energetic Forms of Hydrogen on the Ni(100) Surface

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Adsorbed cyclohexene can be hydrogenated at cryogenic temperatures by both incident gas phase atomic hydrogen and desorbing bulk hydrogen in the presence of adsorbed surface hydrogen on a Ni(100) surface. In both cases, no C–C bond activation is observed, and cyclohexane is the only hydrogenated product. Cyclohexene desorbs without significant reaction from the Ni(100) surface in the presence of coadsorbed surface hydrogen. Selective hydrogenation of adsorbed cyclohexene by bulk hydrogen is observed at 178 K in the leading edge of the bulk hydrogen desorption peak. Hydrogenation of adsorbed cyclohexene by gas phase atomic hydrogen is observed below 140 K. Isotope studies of the hydrogenation mechanism suggest that the hydrogenation of adsorbed cyclohexene by gas phase atomic hydrogen is a sequential process with the first hydrogen adding from the gas phase and the second from the surface. The small amount of benzene observed from adsorbed cyclohexene monolayers indicates that gas phase atomic hydrogen also causes some hydrogen abstraction.

Hydrogen addition to cyclohexene is an interesting model reaction because isomerization, hydrogenolysis, hydrogenation, and dehydrogenation can all occur with this six carbon cyclic system. Catalytic hydrogenation of cyclohexene has been studied previously over supported Ni, Pt, and Pd catalysts using hydrogen pressures above 100 Torr and temperatures above 300 K.[1–5] In typical practice, hydrogenation of olefin molecules is performed over supported Ni catalysts at temperatures in the range of 425–475 K and pressures of 750–5250 Torr.[6] In this work, cyclohexene hydrogenation has been demonstrated on a Ni(100) surface at a low temperature and pressure using either gas phase atomic hydrogen or bulk hydrogen. The data presented here indicate that energetic forms of hydrogen offer an alternate method for inducing hydrogenation in complex molecules which require thermal activation. In addition, hydrogenation induced by energetic forms of hydrogen can be performed under conditions where mechanistic studies are accessible.

Recently, reactions between gas phase atomic hydrogen and adsorbed species have been demonstrated on a number of surfaces. Atomic hydrogen has an additional 52.1 kcal/mol of potential energy and is much more reactive than molecular hydrogen. Hydrogen abstraction from the surface,[7–12] halogen abstraction from the surface,[13–15] and hydrogen addition to the surface[12,16–19] have all been observed in the reaction of gas phase atomic hydrogen with surface adsorbates. Hydrogen *addition* to surface carbon or hydrocarbons has a reaction cross section about 2 orders of magnitude higher than hydrogen *abstraction* from surface hydrocarbons.[10–12] The reactivity trends we observed are consistent with this previous work.

During this work, atomic hydrogen was created on a hot W filament (>2000 K) by dissociation of molecular hydrogen (9.3×10^{-7} Torr). The theoretical limit for the dissociation efficiency of H_2 is 0.3 per collision under the experimental conditions used.[20,21] No W peaks were observed in the Auger electron spectra (AES) even after prolonged H atom exposure, indicating that no significant W contamination of the surface occurs.

In general terms, bulk hydrogen in a Ni crystal has 15 kcal/mol higher potential energy than surface hydrogen.[22] Bulk hydrogen desorbs at a low temperature (180–250 K) from the close packed Ni(111) surface with considerable excess translational energy as indicated by a strongly forward-peaked angular distribution.[23–25] Bulk hydrogen has been shown to react with adsorbed methyl and ethylene on the Ni(111) surface.[26,27] Mechanisms for coupled desorption/diffusion of bulk hydrogen on/in a Ni(111) surface have been recently characterized by our group using mean field modeling of TPD (temperature-programmed desorption).[28]

The properties of desorbing bulk hydrogen have not previously been characterized on the Ni(100) surface. TPD spectra taken from the Ni(100) crystal after exposure to atomic hydrogen at 130 K show a new low-temperature desorption peak at 188 K, in addition to the usual surface hydrogen recombination peak in the 227–430 K temperature range (Figure 1). Similar low-temperature hydrogen desorption peaks have been previously observed as the result of bulk hydrogen desorption from a Ni(111) crystal.[23–25] The new peak at 188 K has never been detected after exposure to molecular hydrogen. The maximum desorption temperature of this peak is independent of peak size. The peak size increases with atomic hydrogen exposure without evident saturation within the range of experiments we have performed (Figure 1). Taken together, these results indicate that bulk hydrogen must cause the desorption peak at 188 K.

Desorbing bulk hydrogen selectively hydrogenates monolayers of cyclohexene to cyclohexane in the presence of adsorbed surface hydrogen (Figure 2). Cyclohexane is formed at the leading edge of the bulk hydrogen desorption peak (178 K). No C–C bond activation occurs during the reaction of adsorbed cyclohexene with bulk hydrogen as indicated by the absence of desorption peaks corresponding to *n*-hexane (*m/e* = 57), methane (*m/e* = 15 and *m/e* = 16), ethane (*m/e* = 30), and propane (*m/e* = 29 and *m/e* = 44). Dehydrogenation leading to benzene formation is not observed. The 78 amu peaks below 210 K are caused by fragmentation of cyclohexene in our mass spectrometer.[29] For a monolayer of cyclohexene, the cyclohexane yield increases with increasing amounts of bulk hydrogen. Our best estimate indicates that the cyclohexane yield is

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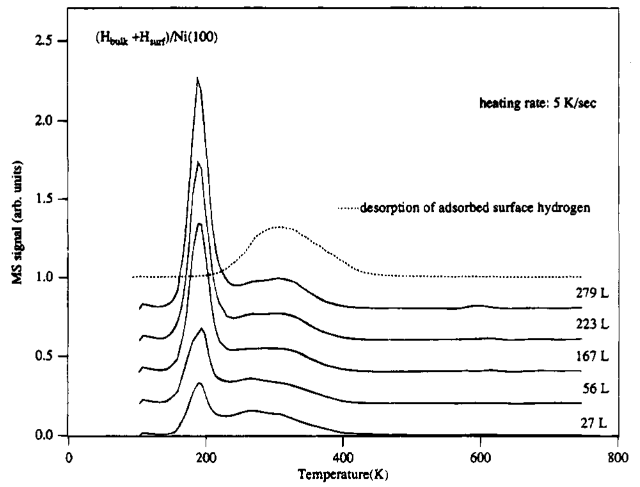

Figure 1. Hydrogen TPD spectra of Ni(100) after exposure to atomic hydrogen. A new desorption peak at 188 K is observed in addition to the surface hydrogen desorption peak.

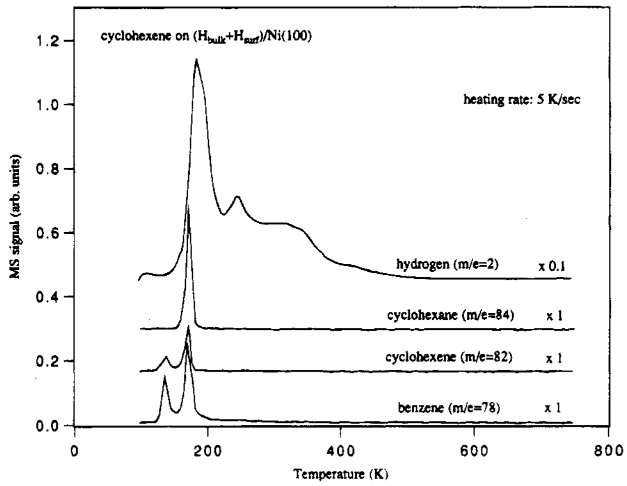

Figure 2. TPD spectra of 1.4 ML of cyclohexene reacted with 10 equivalent monolayers of bulk hydrogen on the Ni(100) surface preexposed to 280 langmuirs of molecular hydrogen.[35] Cyclohexane formation is observed at 178 K.

over 70% when 10 equivalent monolayers of bulk hydrogen react with an adsorbed monolayer of cyclohexene.[30] Multilayer cyclohexene is not hydrogenated by bulk hydrogen, as expected, since multilayers of cyclohexene desorb at 140 K, prior to bulk hydrogen desorption.

Cyclohexene desorbs without significant reaction from the Ni(100) surface when heated in the presence of coadsorbed surface hydrogen (Figure 3). Multilayer cyclohexene ice sublimes at 140 K, and adsorbed cyclohexene desorbs intact at 185 K. The small 84 amu peak at 170–250 K (<1% of desorbing cyclohexene) may be caused by cyclohexane formed at (110) defects[27] or might also be the result of $m + 2$ fragments from desorbing cyclohexene. No dehydrogenation occurs in the presence of coadsorbed surface hydrogen. However, in the absence of coadsorbed surface hydrogen, a large fraction of the adsorbed cyclohexene is dehydrogenated to form benzene on a Ni(100) surface during TPD experiments.[31,32] Thus, coadsorbed surface hydrogen suppresses dehydrogenation of cyclohexene but does not cause substantial cyclohexene hydrogenation.

Bulk hydrogen has substantially higher energy than adsorbed surface hydrogen and a different approach trajectory to the adsorbed cyclohexene. The excess energy of desorbing bulk hydrogen may be used to overcome activation barriers associated with hydrogen addition. Cyclohexene is adsorbed almost parallel to the surface plane.[33] The approach of hydrogen from below adsorbed cyclohexene may decrease hydrogenation activation energies because of stabilizing interactions between the approaching hydrogen atom and the p orbital of cyclohexene. Both of these factors may assist with the rapid and selective hydrogenation reaction caused by bulk hydrogen.

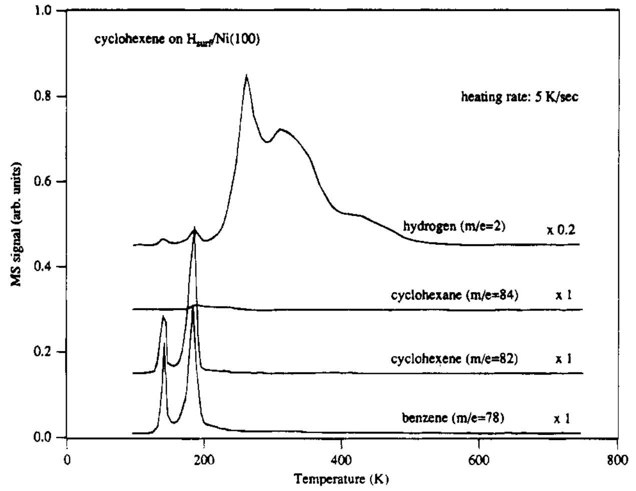

Figure 3. TPD spectra of 1.3 ML of cyclohexene adsorbed on the Ni(100) surface preexposed to 108 langmuirs molecular hydrogen.[35] Cyclohexene desorbs without reaction.

Gas phase atomic hydrogen also hydrogenates cyclohexene to cyclohexane in the presence of surface hydrogen below 140 K as indicated in Figure 4a. Multilayers as well as monolayers of cyclohexene are hydrogenated by incident gas phase atomic hydrogen, suggesting that the hydrogenation may occur through an Eley–Rideal mechanism. Two desorption-limited cyclohexane peaks[31] are observed at 140 and 170 K following hydrogenation. No C–C bond activation is observed as indicated by the absence of noncyclic hydrocarbon products. The desorption-limited benzene peak[34] observed above 350 K indicates that hydrogen abstraction also occurs during the reaction with gas phase atomic hydrogen. Benzene produced undergoes decomposition as well as desorption above 380 K,[34] resulting in the broad hydrogen desorption peak observed above 400 K. The 78 amu peaks below 210 K are caused by fragmentation of cyclohexene in our mass spectrometer.[29]

Reactions with gas phase atomic hydrogen were investigated on a hydrogen-presaturated Ni(100) surface to prevent the decomposition of cyclohexene and to limit the formation of bulk hydrogen. However, a small amount of bulk hydrogen (<0.1 monolayer equivalent) was formed during the exposure to gas phase atomic hydrogen. The small amount of cyclohexane formed by bulk hydrogen at 170 K (Figure 4a) is not significant because the yield decreases with decreasing amounts of bulk hydrogen.[31] For gas phase atomic hydrogen-induced hydrogenation, the estimated cyclohexane yield from adsorbed cyclohexene ranges up to 80%,[30] depending on the exposure time to gas phase atomic hydrogen. Therefore, cyclohexane must be formed primarily by reaction with gas phase atomic hydrogen when adsorbed cyclohexene is exposed to gas phase atomic hydrogen.

Mechanistic studies with isotopic hydrogen suggest that the hydrogenation of adsorbed cyclohexene by gas phase atomic hydrogen is a sequential process with the first hydrogen added from the gas phase and the second from the surface. To elucidate the hydrogenation mechanism, a flux of atomic deuterium was directed onto cyclohexene adsorbed on the hydrogen-saturated Ni(100) surface. Singly deuterated cyclohexane-d_1, not doubly deuterated cyclohexane-d_2, was the main hydrogenation product from this reaction (Figure 4b). There-

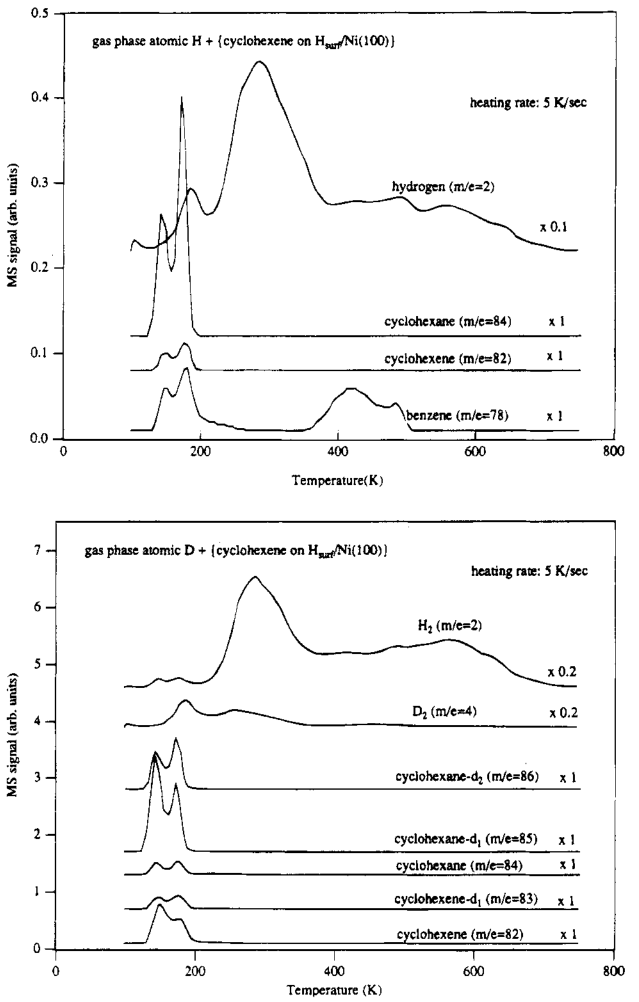

Figure 4. (a, top) TPD spectra taken after an exposure of 141 langmuirs of gas phase atomic hydrogen[35] to 1.7 ML of cyclohexene adsorbed on a hydrogen-presaturated Ni(100) surface. Cyclohexene is hydrogenated to cyclohexane by gas phase atomic hydrogen below 140 K. (b, bottom) TPD spectra taken after an exposure of 139 langmuirs of gas phase atomic deuterium[35] to 3.1 ML of cyclohexene adsorbed on a hydrogen-presaturated Ni(100) surface. Singly deuterated cyclohexane-d_1 is the main hydrogenated product observed.

fore, surface hydrogen appears to be involved in the hydrogenation process, even though surface hydrogen alone cannot hydrogenate cyclohexene. The hydrogenation seems to be initiated by gas phase atomic D to form a deuterated intermediate. Adsorbed surface hydrogen hydrogenates this intermediate to form primarily cyclohexane-d_1 (*m/e* = 85). Cyclohexene-d_1 (*m/e* = 83), cyclohexane (*m/e* = 84), and cyclohexane-d_2 (*m/e* = 86) are also formed in addition to the primary cyclohexane-d_1 reaction product, indicating that hydrogen elimination and hydrogen–deuterium isotope exchange also occur during the reaction. The formation of cyclohexane-d_2 suggests that the deuterated intermediate might be hydrogenated also by a small amount of bulk deuterium and surface deuterium, which was created from long D atom dosing. Differing reaction mechanisms cause differing isotopic ratios in the 140 and 170 K cyclohexane desorption peaks.

In summary, cyclohexene hydrogenation has been demonstrated on a Ni(100) surface at cryogenic temperatures and low pressures using either gas phase atomic hydrogen or bulk hydrogen. These energetic forms of hydrogen offer an alternate method for inducing hydrogenation in complex molecules which require thermal activation.

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(29) During the TPD experiments, the electron energy was 70 eV and the multiplier gain for standard N_2 gas was 10^5. With the QMS used in our experiments, the major peaks observed for cyclohex*ene* are *m/e* = 54 (24%), 67 (100%), 77 (8%), 78 (21%), 79 (13%), and 82 (8%). For cyclohex*ane*, the major peaks are observed at *m/e* = 41 (38%), 55 (37%), 56 (100%), 69 (65%), and 84 (60%).

(30) For the estimation of yield, the ionizer voltage in the QMS was set to 18 V during the TPD experiments to reduce the number of fragments, and the intensities of all fragments detected were added to give the amount for each parent molecule. Cyclohexene and cyclohexane have similar sensitivity in the mass spectrometer we used (Manual for UTI 100C Precision Mass Analyzer; Figures B2, B3, and B4).

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