



# Site-blocking effects of preadsorbed H on Pt(1 1 1) probed by 1,3-butadiene adsorption and reaction

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## ABSTRACT

The influence of hydrogen coadsorption on hydrocarbon chemistry on transition metal surfaces is a key aspect to an improved understanding of catalytic selective hydrogenation. We have investigated the effects of H preadsorption on adsorption and reaction of 1,3-butadiene (H<sub>2</sub>C=CHCH=CH<sub>2</sub>, C<sub>4</sub>H<sub>6</sub>) on Pt(1 1 1) surfaces by using temperature-programmed desorption (TPD) and Auger electron spectroscopy (AES). Preadsorbed hydrogen adatoms decrease the amount of 1,3-butadiene chemisorbed on the surface and chemisorption is completely blocked by the hydrogen monolayer (saturation) coverage ( $\theta_{\text{H}} = 0.92$  ML). No hydrogenation products of reactions between coadsorbed H adatoms and 1,3-butadiene were observed to desorb in TPD experiments over the range of  $\theta_{\text{H}}$  investigated ( $\theta_{\text{H}} = 0.6$ – $0.9$  ML). This is in strong contrast to the copious evolution of ethane (CH<sub>3</sub>CH<sub>3</sub>, C<sub>2</sub>H<sub>6</sub>) from coadsorbed hydrogen and ethylene (CH<sub>2</sub>=CH<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>) on Pt(1 1 1). Hydrogen adatoms effectively (in a 1:1 stoichiometry) remove sites from interaction with chemisorbed 1,3-butadiene, but do not affect adjacent sites. The adsorption energy of coadsorbed 1,3-butadiene is not affected by the presence of hydrogen on Pt(1 1 1). The chemisorbed 1,3-butadiene on hydrogen preadsorbed Pt(1 1 1) completely dehydrogenates to H<sub>2</sub> and surface carbon upon heating without any molecular desorption detected, which is identical to that observed on clean Pt(1 1 1). In addition to revealing aspects of site blocking that should have broad implications for hydrogen coadsorption with hydrocarbon molecules on transition metal surfaces in general, these results also provide additional basic information on the surface science of selective catalytic hydrogenation of butadiene in butadiene–butene mixtures.

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## 1. Introduction

Butadiene (H<sub>2</sub>C=CHCH=CH<sub>2</sub>, C<sub>4</sub>H<sub>6</sub>) is an impurity in C<sub>4</sub> alkene streams produced by steam cracking and it is desirable to remove this product from butadiene–butene mixtures. An ideal process would be to selectively convert butadiene to butene (C<sub>4</sub>H<sub>8</sub>) and avoid forming the completely hydrogenated product, i.e., butane (C<sub>4</sub>H<sub>10</sub>). The hydrogenation of butadiene has been widely studied over supported Pt catalysts [1–6] and Pt single crystals [4,7–13]. Over supported Pt catalysts, hydrogenation of 1,3-butadiene yields *n*-butane (H<sub>3</sub>CCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, C<sub>4</sub>H<sub>10</sub>), 1-butene (H<sub>2</sub>C=CHCH<sub>2</sub>CH<sub>3</sub>, C<sub>4</sub>H<sub>8</sub>) and 2-butene (H<sub>3</sub>CCH=CHCH<sub>3</sub>, C<sub>4</sub>H<sub>8</sub>) simultaneously [2–4]. The selectivity of forming butene over butane is greatly affected by the support material [6]. Hydrogenation of 1,3-butadiene over a Pt(1 1 1) single crystal also produces a mixture of *n*-butane, 1-bu-

tene and 2-butene. Two issues of interest in these catalytic studies are the selectivity toward butene formation and product distribution between butene isomers. Methods to study adsorbed layers and identify surface intermediates during hydrogenation at high pressures on metal single crystals are limited. One approach has been to investigate coadsorption of hydrogen and unsaturated hydrocarbon molecules under UHV conditions in a surface science approach to study hydrogenation at the molecular level.

Coadsorption of hydrogen and ethylene on Pt(1 1 1) has been studied nicely by Zaera and coworkers [14–17]. In those investigations, however, the amount of hydrogen present on the surface,  $\theta_{\text{H}}$ , was always far away from monolayer (saturation) coverages and no comments were made on any influence of H adatoms blocking sites at the surface. Hemminger and coworkers [18,19] studied the dehydrogenation of cyclohexane on Pt(1 1 1) that had been precovered by a saturation coverage of adsorbed hydrogen produced by large H<sub>2</sub> exposures. They observed that preadsorbed H weakened the interaction between Pt(1 1 1) and cyclohexane and the initial dehydrogenation activation energy was lowered by 20%. They reported that H adatoms had no effect on the sticking coefficient of cyclohexane on Pt(1 1 1) at 135 K and did not block cyclohexane

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adsorption. However, Lutterloh et al. [20] using a pyrolytic H atom source, found that chemisorption of benzene was completely blocked at high coverages of preadsorbed H adatoms on Pt(1 1 1) at 125 K. It is interesting to note that the maximum value for  $\theta_{\text{H}}$  on Pt(1 1 1) obtained by exposing  $\text{H}_2$  has been reported to be 0.8 ML [21], and this coverage is difficult to obtain practically (requiring exposures of several hundreds of Langmuirs) because of the low dissociative sticking probability of  $\text{H}_2$  at large values of  $\theta_{\text{H}}$ . This is probably why the amount of preadsorbed H used in most previous studies did not include a saturation (monolayer) coverage. The saturation coverage of H adatoms on Pt(1 1 1) can be increased to  $\theta_{\text{H}} = 0.95$  ML by using a pyrolytic H atom source [22]. Because the absolute coverages in adsorbed hydrocarbon monolayers on Pt(1 1 1) can be quite low,  $\theta_{\text{HC}} = 0.25\text{--}0.1$  ML, it may be important to study the influence of coadsorbed hydrogen at very high coverages otherwise islanding or ensemble effects can allow coadsorbed hydrocarbon molecules to simply avoid interacting directly with the coadsorbed H adatoms. In addition, the role of site blocking effects of preadsorbed H should become more important at high values of  $\theta_{\text{H}}$  than for low ones.

Herein, we describe the results of our investigations of adsorption and reaction of 1,3-butadiene on Pt(1 1 1) surfaces that contain varying amounts of preadsorbed H adatoms up to  $\theta_{\text{H}} = 0.9$  ML by using a pyrolytic H atom source.

## 2. Experimental methods

Experiments were performed in a three-level UHV chamber as described earlier [23]. The Pt(1 1 1) crystal (Atomergic; 10 mm diameter, 1.5 mm thick) was prepared by 1-keV  $\text{Ar}^+$ -ion sputtering and oxygen treatments ( $5 \times 10^{-7}$  Torr  $\text{O}_2$ , 900 K, 2 min) to give a clean spectrum using Auger electron spectroscopy (AES) and a sharp ( $1 \times 1$ ) pattern in low energy electron diffraction (LEED).

A Pt-tube doser was constructed, based on the design of Engel and Rieder [24], and used as a pyrolytic source of gas-phase H atoms. The principal component is a bent Pt tube (1-mm OD, 0.8-mm ID) into which a hole of 0.1-mm diameter was mechanically drilled. The Pt tube was resistively heated to 1275 °C, and water-cooling kept the adjacent Cu block cold. The temperature of the Pt tube was directly measured by an optical pyrometer that was calibrated by the temperature of the Pt(1 1 1) crystal sample, as measured by a Cr/Al thermocouple. The relative accuracy of the pyrometer reading was estimated to be  $\pm 5$  °C. The flux of H atoms obtained from this source at 800 °C and a pressure of  $5 \times 10^{-8}$  Torr in the UHV chamber was  $3 \times 10^{13}$  atoms  $\text{cm}^{-2} \text{s}^{-1}$ . This value was obtained by assuming that the initial sticking coefficient of incident H atoms on Pt(1 1 1) at 100 K was unity and using the H coverage produced from the well-known decomposition of ethylene on Pt(1 1 1) to give an absolute calibration for the  $\text{H}_2$  yield in subsequent TPD measurements [25].

$\text{H}_2$  (Matheson; 99.99%) was introduced via a variable leak valve (Granville–Phillips) into the Pt-tube doser after passing through a liquid-nitrogen cooled, U-tube trap. 1,3-butadiene ( $\text{C}_4\text{H}_6$ , Matheson; 99.5%) was introduced via a microcapillary array doser connected to the gas line through a leak valve. All of the exposures reported herein are given simply in terms of the pressure measured in the UHV chamber by the ion gauge. No attempt was made to correct for the flux enhancement of the gas doser or ion gauge sensitivity. Mass spectrometry performed in the UHV chamber showed no appreciable concentration of impurities in the source gases.

The heating rate was 3.6 K/s in all TPD experiments, and all exposures were given at a sample temperature of 100 K. AES measurements were made with a double-pass cylindrical mirror analyzer (CMA) using a modulation voltage of 4 eV. The electron gun

was operated at 3-keV beam energy and 1.5- $\mu\text{A}$  beam current. Coverages  $\theta_i$  reported in this paper are referenced to the surface atom density of Pt(1 1 1) such that  $\theta_{\text{Pt}} = 1.0$  ML is defined as  $1.505 \times 10^{15} \text{ cm}^{-2}$ .

## 3. Results

TPD was used to probe adsorption and reaction of 1,3-butadiene on clean Pt(1 1 1) at 100 K and surfaces that were precovered with H adatoms following exposures from the pyrolytic H-atom doser. The exposure of 0.24-L 1,3-butadiene was determined in other experiments (not shown) to produce about 1.3 ML of 1,3-butadiene on the Pt(1 1 1) surface at 100 K [26]. Signals at 2, 18, 54, 56, 58, 108, 110 amu were recorded to monitor possible reaction products in TPD, but only  $\text{H}_2$  (2 amu) and  $\text{C}_4\text{H}_6$  (54 amu) were identified as desorbed products. Monitoring with high signal to noise detection for the parent ions of butene (56 amu) and butane (58 amu) indicated no desorption due to hydrogenation of 1,3-butadiene by preadsorbed H on Pt(1 1 1). We note that in previous work under UHV conditions, no hydrogenation products were observed from 1,3-butadiene adsorption on Pt(1 1 1) in the absence of hydrogen [27]. Also, we did not observe any  $\text{C}_8$  coupling products, as monitored by signals at 108 and 110 amu. Desorption spectra for  $\text{C}_4\text{H}_6$  and  $\text{H}_2$  are shown in Figs. 1 and 2, respectively. We also note here that we monitored water coadsorption in all of these experiments because of the low-temperature adsorption requirements. TPD measurements (not shown) that directly compared  $\text{H}_2\text{O}$  TPD following  $\text{H}_2\text{O}$  adsorption on Pt(1 1 1) were used to establish that

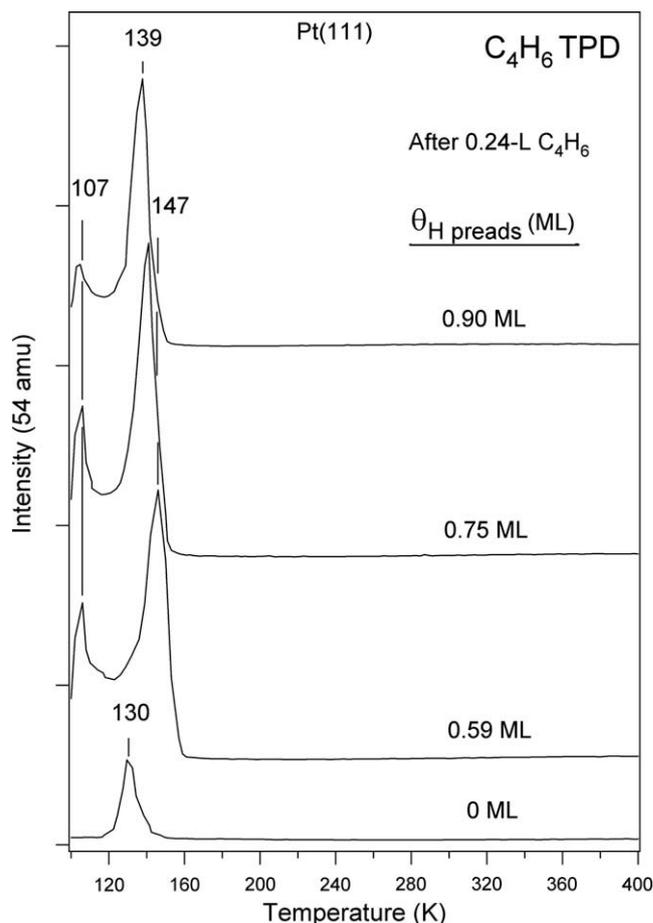
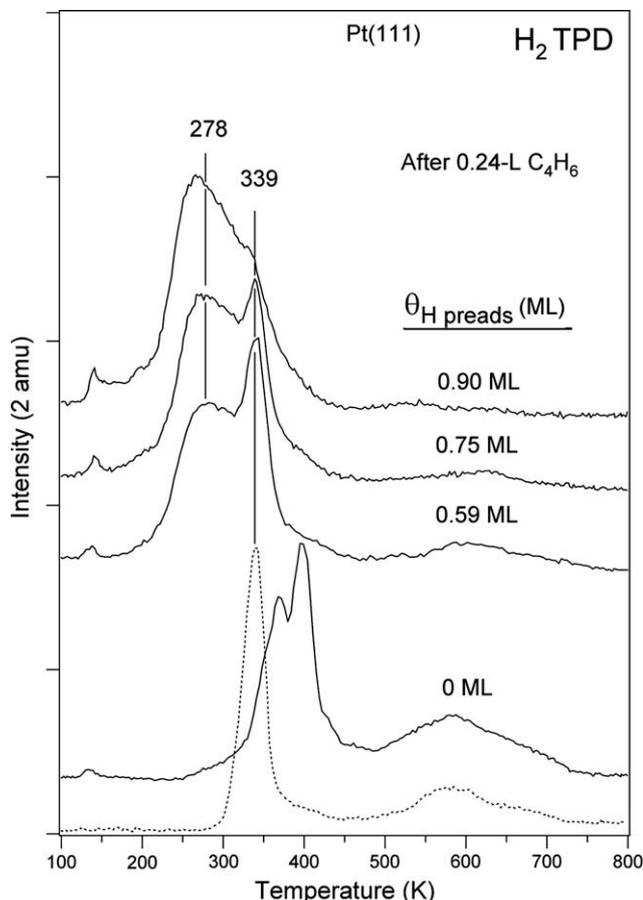


Fig. 1.  $\text{C}_4\text{H}_6$  TPD spectra after 0.24-L 1,3-butadiene exposures on H preadsorbed Pt(1 1 1) at 100 K.



**Fig. 2.** H<sub>2</sub> TPD spectra after 0.24-L 1,3-butadiene exposures on H preadsorbed Pt(1 1 1) at 100 K. (Dash curve is the H<sub>2</sub> TPD spectra after 0.057-L 1,3-butadiene exposures on Pt(1 1 1) at 100 K).

the amount of water coadsorption in these preadsorbed-H experiments was small, ranging from 0.03 to 0.08 ML for all but the largest H atom precoverage of  $\theta_{\text{H}} = 0.9$  ML where  $\theta_{\text{H}_2\text{O}} = 0.13$  ML.

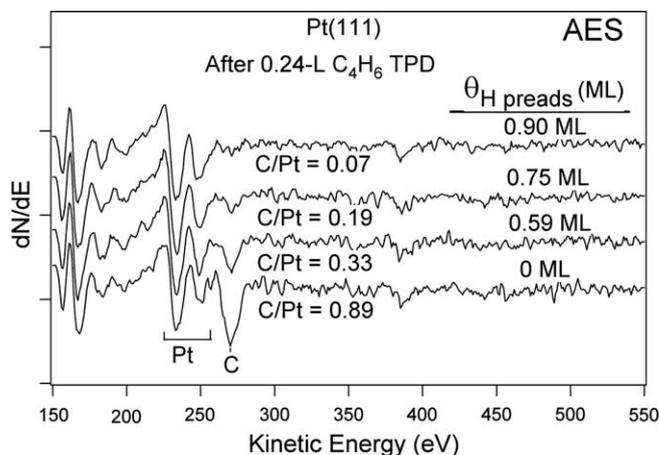
In the absence of preadsorbed H, as shown in the bottom curve of Fig. 1, the 1,3-butadiene monolayer is completely irreversibly adsorbed and no molecular desorption of chemisorbed species occurs. Physisorbed molecules present in the second layer desorb in a low-temperature peak at 130 K [26]. On H-precovered Pt(1 1 1) surfaces, no chemisorbed species desorb and only desorption of physisorbed C<sub>4</sub>H<sub>6</sub> species in a peak at 147–139 K was observed. Butadiene molecules that cannot be accommodated in the monolayer condense into multilayer clusters and desorption from this phase occurs at low coverages in a peak at 107 K [26].

The solid curves shown in Fig. 2 illustrate the effect of preadsorbed hydrogen on hydrogen desorption following butadiene adsorption. The bottom, solid curve was obtained in the absence of any preadsorbed hydrogen, and shows extensive hydrogen desorption from the dehydrogenation of all of the adsorbed butadiene. Preadsorbing H on the Pt(1 1 1) surface induces a new broad H<sub>2</sub> desorption peak at 278 K that arises from desorption rate-limited recombination of H adatoms that desorb as H<sub>2</sub>, as established by H-atom experiments in the absence of butadiene (not shown). In addition, a narrow peak at 339 K was observed, and this peak decreased with an increase in the amount of preadsorbed H. This peak arises from decomposition of a small coverage of 1,3-butadiene in the monolayer, as shown by the dashed curve at the bottom of Fig. 2, which was obtained with no preadsorbed H on the Pt(1 1 1) surface. Evolution of H<sub>2</sub> from decomposition of 1,3-butadiene

occurs in a large peak at 339 K and a smaller feature at 610 K [26] at low coverages, but the H<sub>2</sub> desorption curve depends strongly on the butadiene coverage and the shape gradually evolves toward that of the bottom solid curve at higher coverages of butadiene. The dashed curve enables us to conclude the 339 K peaks in the curves in Fig. 2 are due to hydrocarbon decomposition processes that liberate additional H<sub>2</sub> and that preadsorbed hydrogen decreases the amount of hydrocarbon decomposition, but does not alter the temperature of these processes.

Consistent with these results, the concentration of surface carbon remaining after a TPD experiment, detected by AES, also decreased with an increase in amount of preadsorbed hydrogen. This is shown in Fig. 3, and the carbon AES peak after TPD is nearly eliminated after TPD following 0.24-L 1,3-butadiene on Pt(1 1 1) with 0.90-ML H preadsorbed. We explain these observations by a decrease in amount of chemisorbed 1,3-butadiene, rather than a decrease in the fraction of chemisorbed 1,3-butadiene that dehydrogenates during TPD, with increasing amounts of preadsorbed hydrogen. This explanation is supported by two experimental facts from TPD: (i) Fig. 1 shows that there is no increase in the amount of unreacted butadiene that desorbs from the chemisorbed layer, and (ii) no other hydrocarbon desorption was detected in experiments that searched for a variety of other hydrocarbon products.

Because all chemisorbed 1,3-butadiene molecules decompose to liberate H<sub>2</sub> and form surface carbon, the amount of H<sub>2</sub> generated from decomposition of 1,3-butadiene in TPD can be used to determine the coverage of chemisorbed 1,3-butadiene. This requires a comparison of the measured H<sub>2</sub> TPD peak area to that of a reference H<sub>2</sub> TPD spectrum that corresponds to a known value of  $\theta_{\text{H}}$ . We utilized the H<sub>2</sub> TPD spectrum after ethylene (C<sub>2</sub>H<sub>4</sub>) exposures on Pt(1 1 1) at 300 K to produce 0.25-ML ethylidyne (CCH<sub>3</sub>) [25], in which complete decomposition produces 0.375-ML H<sub>2</sub>, i.e.,  $\theta_{\text{H}} = 0.75$  ML. The result is that the 1,3-butadiene monolayer (saturation) coverage  $\theta_{\text{C}_4\text{H}_6} = 0.15$  ML on clean Pt(1 1 1) [26,28]. The H<sub>2</sub> TPD area resulting from the decomposition of chemisorbed 1,3-butadiene in the coadsorption experiments was obtained by subtracting the H<sub>2</sub> TPD area recorded without adding coadsorbed 1,3-butadiene from the corresponding H<sub>2</sub> TPD area in Fig. 2. These results are shown in Fig. 4. Fig. 4 also gives the result of using the C(272 eV)/Pt(237 eV) peak-to-peak ratio in AES after TPD (Fig. 3) for determining the C<sub>4</sub>H<sub>6</sub> coverage that decomposes during TPD. A C(272 eV)/Pt(237 eV) ratio of 0.89 after TPD of 0.24-L 1,3-butadiene on clean Pt(1 1 1) corresponds to  $\theta_{\text{c}} = 0.60$  ML. Thus, with consistent results from H<sub>2</sub> TPD and AES, the coverage of 1,3-butadiene  $\theta_{\text{C}_4\text{H}_6}$  decreased almost linearly with an increase in precoverage of



**Fig. 3.** AES spectra on Pt(1 1 1) following 0.24-L C<sub>4</sub>H<sub>6</sub> TPD experiment on H preadsorbed Pt(1 1 1).

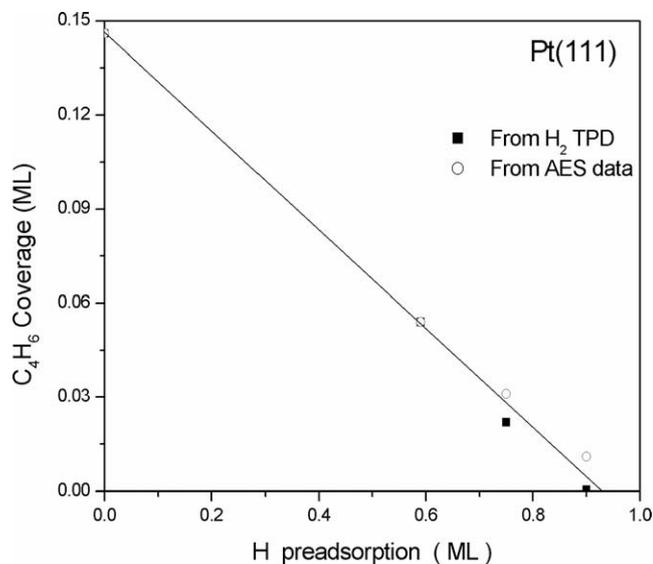


Fig. 4. The influence of preadsorbed H to the C<sub>4</sub>H<sub>6</sub> saturation coverage in the chemisorption layer.

hydrogen  $\theta_{\text{H}}$ . Chemisorption of 1,3-butadiene is totally blocked on Pt(1 1 1) at 100 K by preadsorption of  $\theta_{\text{H}} = 0.92$  ML.

#### 4. Discussion

The two most important findings in this study were that neither butene nor butane desorption due to hydrogenation of 1,3-butadiene by preadsorbed H on Pt(1 1 1) during TPD was observed under any conditions of our experiments, and that chemisorption of 1,3-butadiene was totally blocked on Pt(1 1 1) at 100 K by preadsorption of  $\theta_{\text{H}} = 0.92$  ML. These two observations will be discussed in turn. We note that at high pressure (15 Torr) these products were formed in previous research [13].

In order to understand the different hydrogenation activity for alkenes and dienes, it is instructive to compare in detail the chemisorption of ethylene, 1-butene, and 1,3-butadiene on Pt(1 1 1). Chemisorbed ethylene is di- $\sigma$ -bonded with an adsorption energy of 17 kcal/mol [29]. During heating in TPD, 62% of the ethylene monolayer desorbed, 36% decomposed, and 2% formed ethane [25]. Under UHV conditions, chemisorbed ethylene on Pt(1 1 1) is hydrogenated to ethane at 302 K, corresponding to an activation energy of 18 kcal/mol, in the presence of low hydrogen coverages [30]. Self-hydrogenation [30] can occur in the absence of any specific attempt to cause H coadsorption, and the ethane yield is about 2% of a monolayer. However, this is likely due to small amounts of hydrogen formed from the early stages of ethylene decomposition, low-temperature decomposition at steps, or small amounts of coadsorption from background H<sub>2</sub> adsorption. Addition of hydrogen to form a coadsorbed layer with ethylene on Pt(1 1 1) greatly increased the formation of ethane (up to 50% of the coadsorbed ethylene can be hydrogenated) and decreased the temperature at which ethane desorption occurred in TPD from 302 to 252 K [30]. We calculate that this corresponds to an activation energy for ethylene hydrogenation or ethane formation of 14 kcal/mol by utilizing Redhead analysis [31]. Chemisorbed 1-butene is also di- $\sigma$ -bonded with an adsorption energy of 17 kcal/mol, and has chemistry similar to that of ethylene. During heating in TPD, 53% of the 1-butene monolayer desorbed, 47% decomposed, but no butane was formed [32].

These results for alkenes are in contrast to the behavior that we observed for chemisorbed 1,3-butadiene on Pt(1 1 1) during TPD

studies under UHV conditions. 100% of the 1,3-butadiene monolayer dehydrogenated on the Pt(1 1 1) surface during TPD and no molecular butadiene desorption or self-hydrogenation reaction was observed [26]. The specific addition of a large amount of coadsorbed hydrogen on Pt(1 1 1) still does not induce any hydrogenation reactions that lead to butene or butane desorption. We propose that this qualitatively different behavior from the alkenes can be explained by the larger adsorption energy that butadiene is expected to have over that of alkenes at the surface. The adsorption configuration of chemisorbed 1,3-butadiene on Pt(1 1 1) at 300 K is still unclear, and proposals have been made for tetra- $\sigma$ -bonding [26,28,33] and a 1,4-di- $\sigma$ -bonding configuration in which a new C=C bond is formed in the center of the molecule [34–36]. In either case, we would expect the adsorption energy to be much larger than that of alkene molecules.

Vibrational data for 1,3-butadiene coadsorbed with H on Pt(1 1 1) has not yet been published, but there are reports of vibrational information about the adsorption of butadiene on the clean surface. Avery and Sheppard [27] determined the two most stable configurations for 1,3-butadiene on Pt(1 1 1) are 1,2-di- $\sigma$ -adsorption and 1,2- and 3,4-tetra- $\sigma$ -adsorption as deduced from HREELS studies. Bertolini et al. [34] used HREELS and near-edge X-ray absorption fine structure (NEXAFS) techniques to report that 1,3-butadiene on Pt(1 1 1) adsorbs in a di- $\sigma$  configuration. It was suggested that the presence of coadsorbed H would not affect the adsorption modes for 1,3-butadiene [34]. Theoretical data on the molecular vibrations of butadiene [37] were compared to the experimental HREELS data [27] for 1,3-butadiene adsorption, with the conclusion that the best agreement was for tetra- $\sigma$  adsorption. A strong peak at 780 cm<sup>-1</sup> was said to be correlated with a mode from a minority adsorption geometry as a 1,4-di- $\sigma$ -metallocycle. In DFT studies, Mittendorfer et al. [28] reported the coverage dependence of adsorption modes for 1,3-butadiene on Pt(1 1 1). It was reported that at higher butadiene coverages, there would be a dominant  $\eta$ -2 adsorption geometry in opposition of the  $\eta$ -4 tetra- $\sigma$  bonding configuration due to steric restrictions.

Because no butadiene desorption is observed in TPD, there are no experimental measurements of the desorption activation energy or the adsorption energy. However, we have measured the activation energy for the desorption of 1,3-butadiene on the less reactive (2 × 2)-Sn/Pt(1 1 1) surface alloy to be 21 kcal/mol [26] and we estimate that the value on Pt(1 1 1) is between 26 and 35 kcal/mol. The lower limit comes from the ratio (1.5) between butadiene and 1-butene desorption energies from the (2 × 2)-Sn/Pt(1 1 1) surface alloy and the upper limit comes from assuming tetra- $\sigma$ -bonding on Pt(1 1 1) and that such a configuration would lead to an adsorption energy twice that of 1-butene on Pt(1 1 1). In either case, this stronger bonding to the surface would lead to irreversible chemisorption because of the relatively low energetic barrier to dehydrogenation, which should be about the same as that for ethylene or near 17 kcal/mol. In the past few years, DFT calculations have reported desorption activation energy data for tetra- $\sigma$  bonding of 1,3-butadiene on Pt(1 1 1). At a 1,3-butadiene coverage of 0.25 ML, Mittendorfer et al. reported the desorption activation barrier to be 25 kcal/mol [28]. Valcárel et al. calculated the coverage-dependent activation barrier to range between 37 and 39 kcal/mol [37,38]. So, DFT has provided results consistent with our above estimates.

Hydrogenation of ethylene to form ethane presumably would occur *via* an ethyl intermediate [16]. The barrier for hydrogen addition to chemisorbed butadiene should be about the same as that for ethylene, but the similar barrier sizes for hydrogenation and dehydrogenation makes it much more difficult for the intermediates from butadiene hydrogenation to further hydrogenate to form butene and butane without undergoing dehydrogenation reactions that lead back to butadiene and irreversible H<sub>2</sub> desorption from H

*adatom recombination.* 1-Butene dehydrogenates prior to 345 K and 2-butene dehydrogenates prior to 352 K on Pt(1 1 1) at small coverages [33]. If the barriers to hydrogenation and dehydrogenation of the intermediates involved are similar, but the adsorption energy of the reactant molecule is larger, then thermal reactions will disfavor molecular desorption.

Forming a complete H-adatom monolayer on Pt(1 1 1) completely blocks subsequent chemisorption of benzene [20]. Consistently, we also recently observed that adsorption of ethylene was greatly decreased by the presence of 0.6-ML H on Pt(1 1 1) [39]. 1,3-butadiene has a much stronger interaction with Pt(1 1 1) than ethylene (18 kcal/mol) and comparable or stronger interaction than benzene (28 kcal/mol) and its chemisorption is still blocked by preadsorbed H. These results predict that chemisorption of most hydrocarbon molecules will be blocked by high coverages of preadsorbed H. Coadsorbed H adatoms may block chemisorption of 1,3-butadiene, and other hydrocarbon molecules, by simple repulsive interactions. Fig. 5 shows a schematic drawing showing side views of 1,3-butadiene, ethylene, and benzene adsorption on an H-precovered Pt(1 1 1) surface and clean Pt(1 1 1). In constructing this drawing, the van der Waals radii for H adatoms and the hydrocarbon molecules were used. The vertical positions of the adsorbed species were determined by using either experimentally measured values or theoretical calculations of these numbers. Low-energy recoil scattering [40] indicates that H adatoms occupy *fcc* 3-fold hollow sites and are located 1.2 Å above the first layer of Pt atoms. The C–Pt distances in ethylene [41] and benzene [42] were obtained from recent DFT calculations. The value for 1,3-butadiene was assumed to be the same as that of ethylene for Fig. 5. This schematic drawing, despite its limitations, clearly shows that *non-bonding, repulsive, van der Waals interactions between coadsorbed H adatoms and any of these unsaturated hydrocarbon molecules will not allow for a molecule–Pt distance that is required for covalent overlap and strong chemisorption bonding with Pt atoms at the surface.* This contact leads to an increase in the adsorbate–surface distance on H-preadsorbed Pt(1 1 1) by 1.3–1.4 Å in comparison with that on clean

Pt(1 1 1). This increased distance makes it impossible for the hydrocarbon adsorbates to form chemical bonds with Pt atoms at the surface. However, there still remains an appreciable polarization interaction that stabilizes these hydrocarbons in the adsorbed layer far over that involved in the hydrocarbon condensed phase, and this leads to desorption of 1,3-butadiene at 140–150 K in Fig. 1.

At low coverages of coadsorbed H, islanding of the hydrogen or hydrocarbons into small domains will allow these coadsorbates to simply avoid interacting directly with each other. Displacement of the coadsorbed H adatoms to adjacent adsorption sites will also enable these coadsorbates to avoid large repulsive interactions. Both of these phenomena should be dependent on adsorbate coverages and the temperature. Thus, strong site-blocking effects by H adatoms are expected to be less important at low coverages and high temperatures.

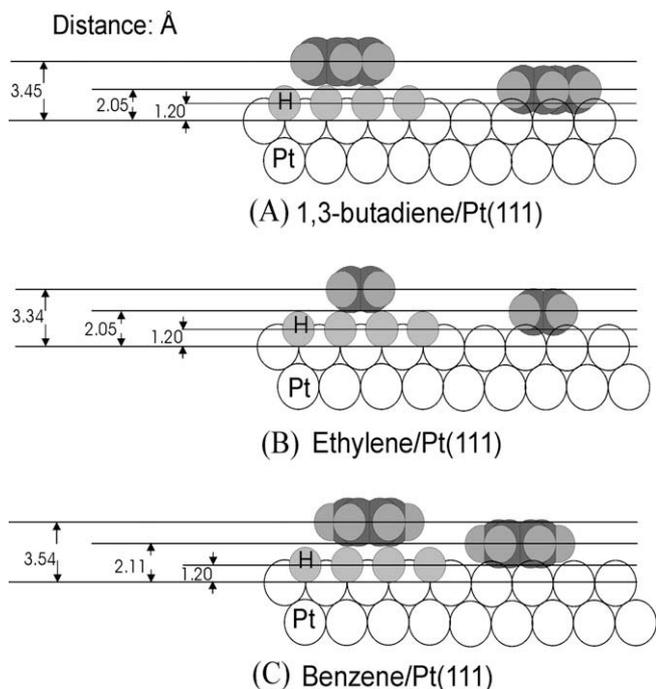
A change in the electronic structure of Pt(1 1 1) may also play a role in the elimination of chemisorption of 1,3-butadiene and other hydrocarbons by coadsorbed H. The Pt–H bond dissociation energy  $D(\text{Pt–H})$  for chemisorbed H adatoms on Pt(1 1 1) is 61.5 kcal/mol [16]. This is a strong polar-covalent bond and this suggests that preadsorbed H could have a significant effect on the electronic structure of Pt(1 1 1). Lutterloh et al. [20] argued that preadsorbed H eliminates the empty metal *d* states on Pt(1 1 1), which are critical for  $\sigma$ - and  $\pi$ -donation, and that this explained why preadsorbed H blocked the chemisorption of benzene. While this undoubtedly plays a role, Fig. 5 illustrates that a simple site-blocking effect of preadsorbed H on Pt(1 1 1) is all that is needed to explain these results. *This should be a general effect with broad applicability to the chemisorption of other organic molecules on other transition metal surfaces.*

## 5. Conclusions

Coadsorbed H adatoms have a strong influence on the coverage of chemisorbed 1,3-butadiene  $\theta_{\text{C}_4\text{H}_6}$  on Pt(1 1 1) at 100 K.  $\theta_{\text{C}_4\text{H}_6}$  decreases linearly with increasing coverages of preadsorbed H on Pt(1 1 1) and chemisorption of 1,3-butadiene is completely blocked at  $\theta_{\text{H}} = 0.92$  ML. This *site-blocking effect of preadsorbed H* can be explained by a simple argument involving repulsive interactions between coadsorbed H and the hydrocarbon coadsorbate, and thus this observation should be a general one applicable to other organic molecules on other transition metal surfaces.

However, other than reducing the amount of chemisorbed species, the presence of coadsorbed H adatoms did not alter the chemistry of chemisorbed 1,3-butadiene on Pt(1 1 1). In the absence of any coadsorbed H adatoms, 1,3-butadiene completely dehydrogenates on Pt(1 1 1) to liberate only  $\text{H}_2$  and form surface carbon upon heating in TPD. Significantly, *no hydrogenation reaction was observed between large amounts of coadsorbed H adatoms* ( $\theta_{\text{H}} = 0.6$ – $0.9$  ML) and 1,3-butadiene, even though extensive hydrogenation of coadsorbed layers of H and ethylene on Pt(1 1 1) has been reported. This can be explained by a stronger bonding interaction between 1,3-butadiene and Pt(1 1 1) that makes it much more difficult for the intermediates from butadiene hydrogenation to further hydrogenate to form butene and butane without undergoing dehydrogenation reactions that lead back to butadiene and irreversible  $\text{H}_2$  desorption from H adatom recombination.

These results also provide additional basic information on the surface science of selective catalytic hydrogenation of butadiene in butadiene–butene mixtures. For example, the Pt surface bonds dienes too strongly to be a good diene hydrogenation catalyst, and so Pt should be modified to reduce this interaction. This commonly occurs by alloying Pt with a second, less-reactive metal, or surface carbonaceous deposits formed under actual catalytic conditions may also play this role.



**Fig. 5.** Side view of 1,3-butadiene (a), ethylene (b) and benzene (c) adsorption on Pt(1 1 1) and H preadsorbed Pt(1 1 1).

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