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The Importance of Transient States at Higher Coverages in Catalytic Reactions

Matthew Neurock,*,[†] Venkataraman Pallassana,[†] and Rutger A. van Santen[‡]

Contribution from the Department of Chemical Engineering, School of Engineering and Applied Science, University of Virginia, Thornton Hall, Charlottesville, Virginia 22903, and Schuit Institute of Catalysis, Department of Inorganic Chemistry, Technical University of Eindhoven, Eindhoven, The Netherlands

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Abstract: DFT-GGA periodic slab calculations were used to examine the adsorption and hydrogenation of ethylene to a surface ethyl intermediate on the Pd(111) surface. The reaction was examined for two different surface coverages, corresponding to (2×3) [low coverage] and ($\sqrt{3}\times\sqrt{3}$)R 30° [high coverage] unit cells. For the low coverage, the di-σ adsorption of ethylene (−62 kJ/mol) is 32 kJ/mol stronger than the π-adsorption mode. The intrinsic activation barrier for hydrogenation of di-σ bonded ethylene to ethyl, for a (2×3) unit cell, was found to be +88 kJ/mol with a reaction energy of +25 kJ/mol. There appeared to be no direct pathway for hydrogenation of π-bonded ethylene to ethyl, for low surface coverages. At higher coverages, however, lateral repulsive interactions between adsorbates destabilize the di-σ adsorption of ethylene to a binding energy of −23 kJ/mol. A favorable surface geometry for the ($\sqrt{3}\times\sqrt{3}$)R 30° coverage is achieved when ethylene is π-bound and hydrogen is bound to a neighboring bridge site. At high coverage, the hydrogenation of di-σ bound ethylene to ethyl has an intrinsic barrier of +82 kJ/mol and a reaction energy of −5 kJ/mol, which is only slightly reduced from the low coverage case. For a ($\sqrt{3}\times\sqrt{3}$)R 30° unit cell, however, the more favorable reaction pathway is via hydrogenation of π-bonded ethylene, with an intrinsic barrier of +36 kJ/mol and an energy of reaction of −18 kJ/mol. This pathway is inaccessible at low coverage. This paper illustrates the importance of weakly bound intermediates and surface coverage effects in reaction pathway analysis.

Introduction

The analysis of nearly every catalytic mechanism centers around the spectroscopic identification of plausible reaction intermediates. It has long been suggested that what is often observed by spectroscopic methods are the most stable surface intermediates, which may or may not be the active species in the mechanism. In many cases, these indeed are kinetically important, but there is now compelling evidence that, under some conditions, these intermediates may merely be spectators. Using Sum Frequency Generation (SFG) techniques at higher pressures, Somorjai and co-workers[1,2] have recently shown that while the di-σ bound ethylene species is energetically the most favorable adsorption state on Pt(111), the π-bound ethylene is likely the precursor for hydrogenation. This was deduced by following the changes in intensity of the C−H stretching frequencies of ethylidyne and di-σ and π-bound ethylene.[1] It was found that increasing the surface coverage of ethylidyne shuts down the adsorption sites for di-σ bound ethylene, but hardly influenced the surface coverage of the π-bonded ethylene intermediate. Since the ethylene hydrogenation turn-over rate was found to be independent of the surface ethylidyne coverage, it was argued that di-σ bound ethylene is unlikely to be the key intermediate for ethylene hydrogenation. This observation was also supported by Zaera and co-workers, who demonstrated that the hydrogenation of ethylene to ethyl on Pt(111) is favored at high coverage, where the transition from di-σ bonded ethylene to π-bonded ethylene is relatively easy.[3,4] The weakly bound ethylene species has also been proposed as the reactive intermediate for hydrogenation on other metal surfaces,[5] such as Fe(100)[6] and Pd.[7−9]

These results present an interesting challenge for ab initio theory. Most of the theoretical efforts to date have focused on establishing the most stable surface species and then computing the activation barriers from this state. Theoretical calculations are almost always carried out for the ideal low surface coverage conditions. Herein, we demonstrate that the more reactive species can be one that is relatively weakly bound to the surface. These species are found to be reactive only at higher coverage conditions. At lower coverage, they desorb or are converted into the more stable surface intermediates before they react. Although the results discussed here were carried out for ethylene hydrogenation over Pd(111), they likely have important consequences to a large number of other reaction systems that are carried out at higher surface coverage.

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* To whom correspondence should be addressed.

[†] University of Virginia.

[‡] Technical University of Eindhoven.

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In this paper, we perform first-principle density functional (DFT) calculations to demonstrate that at low surface coverages, ethylene distinctively hydrogenates from the more stable di-σ bound ethylene surface intermediate. At higher surface coverages, however, the π-bound mode provides a more favorable reaction channel for ethylene hydrogenation.

Computational Methods

All calculations were carried out using periodic DFT methods. The surface was modeled using three layers of Pd to mimic Pd(111) along with a vacuum region of 11.25 Å above the surface. Subsequent calculations on 4–5 layer slabs indicate that the energies changed by less than 1 kcal/mol, by increasing the number of metal layers beyond three.[10] Both the $(\sqrt{3}\times\sqrt{3})R$ 30° and (2×3) unit cells were used to model ethylene and hydrogen surface coverages. All calculations were performed using self-consistent Perdew Wang 91 generalized gradient (GGA) corrections to the Vosko-Wilk-Nusair LDA exchange-correlation energy.[11–13] Scalar relativistic calculations were incorporated through the use of Vanderbilt ultrasoft pseudopotentials.[14] The plane wave basis set used to expand the valence eigenstates had a maximum kinetic energy of 30 Rydberg. Eighteen Chadi-Cohen special k-points were used to sample reciprocal space in the first Brillouin zone.[15] The top two layers of the palladium surface were allowed to relax whereas the bottom layer was constrained to the bulk structure of Pd. The activation barriers were found using the nudged-elastic band approach, whereby a finite number of points are chosen along the reaction coordinate and the energy minimized along all directions normal to the reaction coordinate. Further information on the calculation procedure can be found elsewhere.[16]

Results and Discussion

Low coverage adsorption of atomic hydrogen on Pd(111) was modeled by optimizing hydrogen in the 3-fold fcc hollow site for a (2×3) unit cell. Subsequently, the adsorption of ethylene in a neighboring site was examined for both the π and di-σ adsorption modes. Both binding modes of ethylene are energetically stable on Pd(111). For the low coverage case, the di-σ adsorption state (−62 kJ/mol) was found to be 32 kJ/mol more stable than the π-bound state (−30 kJ/mol).[16,17] The DFT-computed adsorption energy for di-σ bound ethylene (−62 kJ/mol) at low coverage is in good agreement with the experimental estimate (−59 kJ/mol) based on Temperature-Programmed-Desorption (TPD) experiments of ethylene on Pd(111).[18]

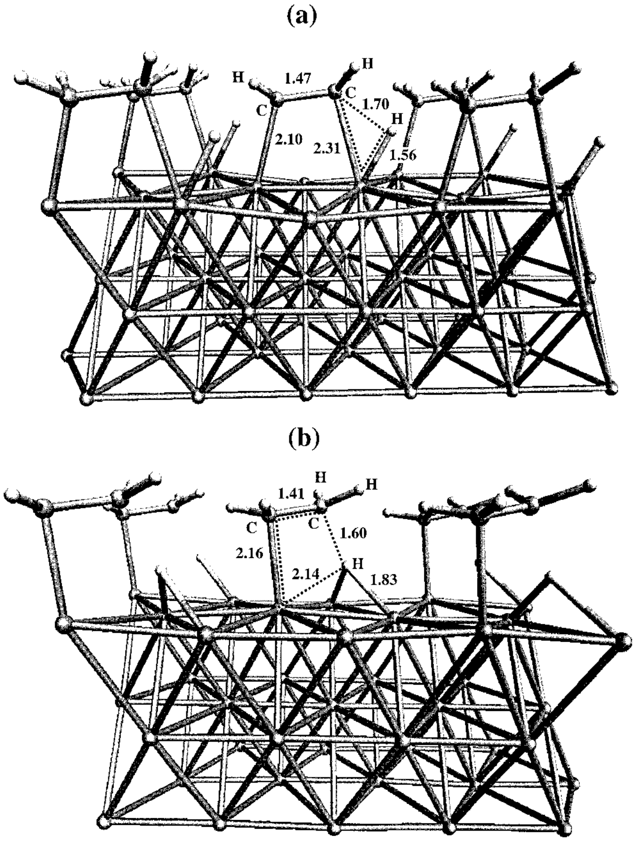

Figure 1. Periodic DFT-computed transition state geometry for the hydrogenation of (a) di-σ bound ethylene on Pd(111) and (b) π-bound ethylene to the surface ethyl intermediate on Pd(111), for $(\sqrt{3}\times\sqrt{3})R$ 30° surface coverages.

The transition state (TS) for ethylene to hydrogenate from the di-σ bound mode for the low coverage (2×3) surface structure is shown in Figure 1a. The transition state geometry and the activation barrier for C−H bond activation of ethyl (+63 kJ/mol), reported here using periodic slab calculations, were found to be quite similar to those we previously determined using DFT cluster calculations (+69 kJ/mol).[16,17,19] This indicates that the (2×3) super-cell provides a good representation of the low coverage situation. It also helps verify that the plane-wave basis and pseudopotentials used in the periodic slab calculations provide structural and energetic results comparable to the traditional Gaussian orbital basis sets used in the cluster calculations. The three-center (Pd−C−H) transition state involves breaking of the metal−hydrogen and metal−carbon bonds, along with the concerted insertion of hydrogen into the metal−carbon bond (Figure 1a). The TS is early along the reaction coordinate for C−H bond formation. A more complete description of the structural features and the electronic factors that govern this step are provided elsewhere.[16,19,20] Attempts to isolate the transition state for ethylene hydrogenation from the π-bound mode, however, failed to locate a transition state. As hydrogen approached the π-bound ethylene, strong lateral repulsive interactions between ethylene and hydrogen forced ethylene into the di-σ adsorption state. At low surface coverage, π-bound ethylene easily translates along the surface to form the energetically more stable di-σ surface complex without undergoing hydrogenation. This process is unlikely to have a significant barrier as the lateral repulsive interactions at low coverage alone drive the change in adsorption mode. Hydrogenation from the di-σ adsorption state therefore appears to be the only reaction path available at low coverage. The energetics for this process are shown in Figure 2a. Ethylene hydrogenation is favored at low coverage wherein the *apparent activation barrier* for hydrogenation is only +26 kJ/mol. For a Langmuir−Hinshelwood mechanism, at low surface coverage of ethylene

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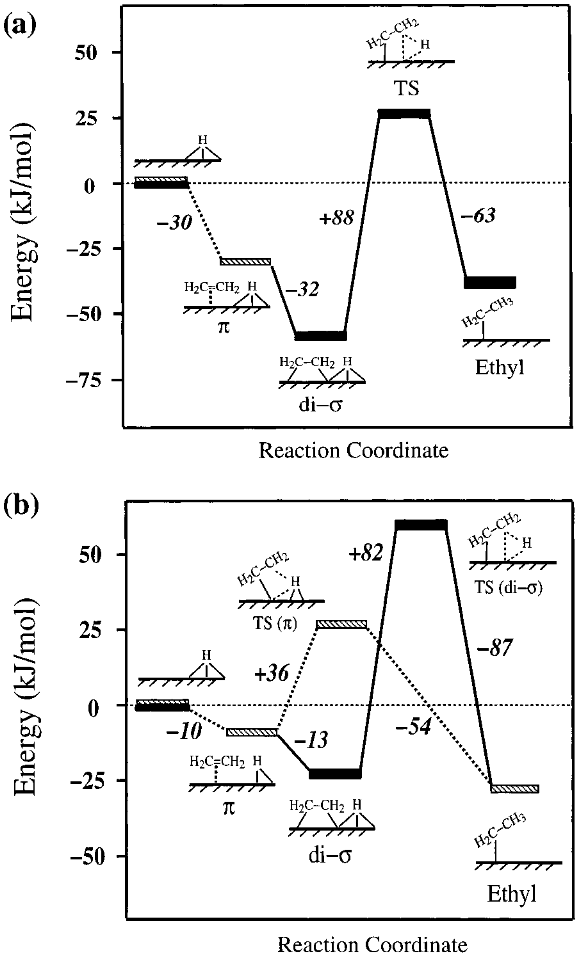
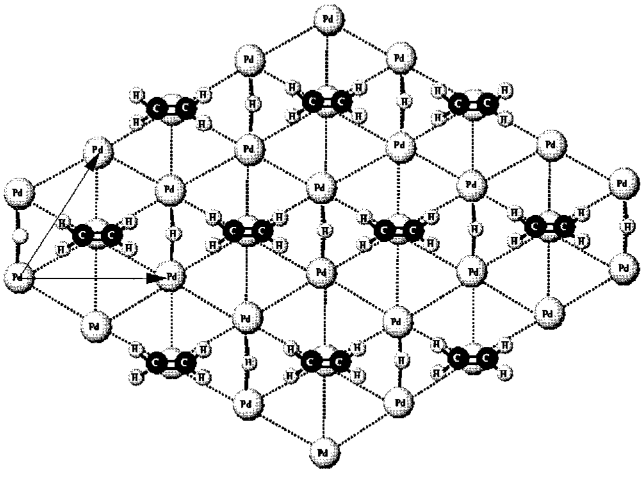


Figure 2. DFT-computed reaction energy profiles for ethylene hydrogenation to a surface ethyl intermediate on Pd(111): (a) (2×3) periodic adsorption of ethylene and atomic hydrogen (*low coverage*) and (b) $(\sqrt{3}\times\sqrt{3})$ periodic adsorption of ethylene and hydrogen (*high coverage*). The solid lines depict the pathway via di-σ bonded ethylene. The dashed lines correspond to ethylene hydrogenation via the π-bonded intermediate.

Chart 1



the energy of adsorption (−62 kJ/mol) serves to lower the intrinsic barrier from the surface (+88 kJ/mol) to an apparent barrier of +26 kJ/mol.

The coadsorption of ethylene and hydrogen at high coverage was modeled using a $(\sqrt{3}\times\sqrt{3})R$ 30° unit cell. In the presence of $(\sqrt{3}\times\sqrt{3})R$ 30° coverage of hydrogen, lateral repulsive interactions between di-σ bound ethylene and hydrogen weaken the di-σ binding energy of ethylene (−62 kJ/mol) by 39 to −23 kJ/mol. These repulsive interactions, albeit smaller in magnitude, are also present for π-adsorption of ethylene. The π-bound species, however, require only a single metal atom adsorption site making it more flexible than the di-σ intermediate which requires two metal atom sites. At the $(\sqrt{3}\times\sqrt{3})R$ 30° coverage, the repulsive surface interactions force hydrogen into the bridge site (see Chart 1). In this configuration, there is no metal atom sharing between hydrogen and π-bonded ethylene and therefore no lateral repulsive interactions. In fact, the π-binding energy of ethylene on a surface covered by $(\sqrt{3}\times\sqrt{3})R$ 30° bridge-bound hydrogen was determined to be −42 kJ/mol, which is 12 kJ/mol stronger than the isolated π-bound state. This can be described in terms of simple bond order conservation, which indicates that if two adsorbates sit at nearest-neighbor sites without sharing the same metal atoms the through-metal lateral interactions are likely to be attractive. For $(\sqrt{3}\times\sqrt{3})R$ 30° coverage, it is not possible to coadsorb di-σ bound ethylene and bridge (or 3-fold) bound hydrogen without sharing surface metal atoms. Metal atom sharing by adsorbates usually leads to lateral repulsive interactions, resulting in a weaker chemisorption energy for both adsorbates.

The reaction coordinate for hydrogenation of di-σ bound ethylene was reanalyzed for the high coverage scenario i.e., $(\sqrt{3}\times\sqrt{3})R$ 30° unit cell. The transition state geometry for hydrogenation of di-σ bound ethylene is almost identical with the one determined for the low coverage (2×3) unit cell, as depicted in Figure la. There are, however, noticeable differences in the energetics of this step. As there are fewer metal−adsorbate bonds at the product state as compared to the reactant state, the lateral adsorbate−adsorbate repulsive interactions are highest at the reactant state and minimal at the product ethyl state, for the higher $(\sqrt{3}\times\sqrt{3})R$ 30° coverage. As a consequence, the overall reaction energy for coupling of ethylene and hydrogen to form ethyl becomes much more favorable as the reaction energy shifts from being +25 kJ/mol endothermic for the low coverage (2×3) case to −5 kJ/mol exothermic for the high coverage $(\sqrt{3}\times\sqrt{3})R$ 30° case. Since the metal−ethylene bond strength is weaker at high coverage because of repulsive interactions, the insertion of hydrogen into the metal−carbon bond has a slightly lower intrinsic activation barrier (+82 kJ/mol) as compared to the low coverage scenario (+88 kJ/mol).

The more dominant reaction pathway at higher coverage, however, is via hydrogenation of π-bound ethylene. At higher coverages, ethylene becomes pinned in a π-bound state between hydrogen and other surface intermediates and therefore cannot translate to a neighboring site to convert to the di-σ intermediate. As the bridge bound hydrogen approaches the π-bound ethylene species, it encounters slight repulsive interactions. The repulsive interactions, however, are not strong enough to force ethylene off the surface. The reaction proceeds via the "slip" mechanism, whereby ethylene slides upward to form a "five-center like" transition state between the central metal atom, the α and β carbon atoms, the hydrogen atom, and two adjacent Pd atoms (see Figure 1b). This "slip" mechanism was first proposed by Thorn and Hoffmann[21] for ethylene hydrogenation over a HPt-$(PH_3)_2$ homogeneous complex. Siegbahn[22] and Morokuma[23] later extended these ideas using ab initio calculations to compute the barriers for the ethylene slip mechanism for single metal

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atom complexes. The "slip" mechanism, however, has never been discussed for hydrogenation of ethylene on a metal surface.[23] It is important to note that the TS described here (see Figure 1b) is somewhat different from the TS proposed by Siegbahn[22] for hydrogenation of π-bound ethylene over a single metal atom center, in that three metal atoms are involved in stabilizing the TS. We explicitly examined the "four-center" TS proposed by Siegbahn for the single metal atom PdH_2 cluster,[22] and found it to be highly unfavorable on Pd(111), for both high and low surface coverage. We find a much lower barrier if we allow neighboring metal atoms to participate in the reaction ensemble by stabilizing the hydrogen atom inserting into the olefin. This is seen in Figure 1b whereby the classical transition state proposed for the homogeneous mechanism is now different because it is stabilized over three surface Pd atoms. Note that the Pd−H distance of 2.14 Å is significantly longer than the normal Pd−H distance of 1.8 Å, making the TS somewhat different from the "four-center" transition state proposed by Siegbahn[22] for olefin hydrogenation over a single metal atom center. The Pd−C distance at the TS (2.16 Å) is slightly shorter than that for π-bound ethylene on Pd(111) (2.2 Å). The transition state is thus more "five-center like" on the periodic Pd(111) surface.

The higher coverage forces ethylene and hydrogen into less favorable π and bridge adsorption sites, respectively. Hydrogenation of ethylene from this π-bound state at high coverage on Pd(111) is much more facile. The intrinsic activation barrier calculated here is now only +36 kJ/mol, which is significantly lower than that determined for the high coverage hydrogenation of di-σ bound ethylene (+82 kJ/mol). We assume that at high coverage both di-σ and π-bound ethylene are in equilibrium with gas-phase ethylene. At higher coverages of ethylene, the intrinsic activation barrier is equivalent to the apparent activation barrier since the reference state is now the adsorbed state. The +36 kJ/mol barrier reported here is consistent with experimental findings which indicate that ethylene hydrogenation barriers on well-defined surfaces, foils, and supported metal particles are all within the range of 36 to 50 kJ/mol.[9,24−26] This pathway is only accessible for high surface coverage conditions. In addition, it requires at least three metal atom centers and is therefore inaccessible for the single metal atom homogeneous catalysts.

Conclusions

In this paper, we have demonstrated that strong repulsive interactions between the adsorbates at high coverage weaken the metal−C and metal−H bonds, allowing for facile insertion of H into the metal−C bond, thus lowering the activation barrier. We see the same effect for hydrogenation over Pd(111) in the presence of subsurface hydrogen. Subsurface hydrogen weakens the interaction of adsorbates with the metal surface, thus lowering the intrinsic activation barrier for hydrogenation. The general conclusion is that *weakening the metal−adsorbate bond strength will lower the intrinsic activation barrier for hydrogenation as well as other coupling reactions.* The converse holds true for bond dissociation processes where *strengthening* the adsorbate−metal bond generally lowers the activation barrier.[20,27−31] This is evident if we examine the reverse barriers for C−H bond breaking of ethyl to form di-σ ethylene. At the lower (2×3) coverages, the barrier is only +63 kJ/mol as compared to +87 kJ/mol for the higher $(\sqrt{3}\times\sqrt{3})R$ 30° surface coverage [see Figure 2, a and b].

The results presented here illustrate the importance of surface coverage effects on the intrinsic activation barriers and hence the controlling reaction mechanism. It suggests that caution must be exercised in determining catalytic reaction pathways based on information collected for the most stable adsorption intermediates alone. The less stable surface species may in fact be the kinetically significant reaction intermediates and must not be discounted during mechanism elucidation.

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