Pathways for dissociative ethane chemisorption on Pt{110} (1 × 2) using density functional theory

A.T. Anghel, D.J. Wales, S.J. Jenkins, D.A. King *

Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK

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Abstract

Accurate transition states and pathways for gaseous C₂H₆ and surface-adsorbed C₂H₅ dehydrogenation on Pt{110} (1 × 2) have been characterised. The electronic structure is treated within a density functional theory framework, and the transition states are refined using hybrid eigenvector-following with variational eigenvector refinement and tangent space minimisation.

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The use of heterogeneous metal-based catalysts offers the possibility of converting alkanes to more useful, reactive forms, as well as producing synthesis gas (syngas), which is a mixture of CO and H₂. A two-step process, involving both steam reforming and the water gas shift reaction, is currently employed in the conversion of methane to syngas [1]. The catalytic partial oxidation (CPO) of alkanes presents the possibility of an alternative, less energy intensive and more direct route to syngas. Platinum is the active catalyst in this process [3], for which the rate-determining step is believed to be the cleavage of the first C–H bond on the metal surface catalyst [2]. The H₂ thus produced is a versatile feedstock for ammonia synthesis, methanol production, the generation of higher-weight hydrocarbons via the Fischer–Tropsch synthesis reaction, or for clean electricity production with high efficiency in fuel cells [4,5]. Furthermore, low contact time, high temperature reactions of alkanes on palladium, platinum and rhodium have recently emerged as an important technology [6]. Ethane, propane and butane are dehydrogenated to their respective unsaturated hydrocarbons for contact times of a few milliseconds with high selectivity. The temperatures employed are above 1200 K for which Weaver et al. [8] have estimated the surface lifetimes for ethane, propane, and butane to be 5 × 10⁻¹² s, 1 × 10⁻¹¹ s and 3 × 10⁻¹¹ s, respectively. These short lifetimes emphasise the importance of understanding the nature of reactive gas-surface collisions between alkanes and a reactive metal surface in more detail. Our results may also be relevant for studies of nanotube growth by chemical vapour deposition [7].

So far, there have been relatively few experimental studies on the dissociation of ethane and higher alkanes at metal surfaces. C₂H₆ dissociation has been considered on Ir{110} [9–11], Pt{111} [12,13] and Pt{110} [14,15] and found to be more complicated than for CH₄. The present work reports theoretical results for ethane dehydrogenation on the corrugated, missing-row reconstructed Pt{110} (1 × 2) surface. Our study has characterised two distinct transition states (TS) for the initial dehydrogenation of weakly physisorbed C₂H₆ to C₂H₅, and two TS for the subsequent dehydrogenation of C₂H₅ to H₂C–CH₂ and to HC–CH₃. The stationary points have been refined to high precision using hybrid eigenvector-following with variational eigenvector refinement and tangent space minimisation. Our method finds transition states by taking uphill steps along the lowest eigenvalue of a starting structure, whilst minimis-
ing in the tangent space [16,17]. This approach requires
precise gradients at each step. The Hessian eigenvector
corresponding to the unique negative eigenvalue at the
TS provides us with a reaction coordinate. Approximate
steepest-descent paths were calculated for each TS using
energy minimisation following small displacements par-
allel and anti-parallel to this coordinate.

Density functional theory calculations were per-
formed using the CASTEP code [19]. The parameters em-
ployed have been described in detail elsewhere [20].

C2H6 and C2H5 dehydrogenation were investigated on
Pt\{110\} (1 x 2) at ridge atop surface sites only, where
C2H5 adsorption was found to preferentially take place.
A coverage of 0.25 monolayers with respect to the cor-
responding unreconstructed (1 x 1) phase was employed.
Initial TS guesses were obtained using constrained min-
imisation. The four TS candidates (two for C2H6 dehy-
drogenation and two for C2H5 dehydrogenation) thus
characterised were then optimised properly by hybrid
eigenvector-following methods, using the OPTIM pro-
gram [16–18]. In this stage of refinement the energy de-
crease for the four stationary points, TS1–TS4, was 0.1
and 0.2 eV for C2H6 dehydrogenation, and 0.004 and
0.017 eV for C2H5 dehydrogenation. Energy profiles
for the corresponding approximate steepest-descent
pathways that lead downhill to the connected local min-
ima are shown in Fig. 1, whilst the energetics are sum-
marised in Table 1. Snapshots along the four
pathways are given in Fig. 2. The path length reported
in Fig. 1 is the integrated path length along the approx-
imate steepest-descent paths, which is a well defined ge-
ometrical property of the potential energy surface.
Geometrical details of the stationary points are provided
in Fig. 3.

For TS1 and TS2 we do not expect the DFT ap-
proach to give an accurate account of the weakly phys-
isorbed minima, because dispersion is not treated
correctly within this framework. The ethane geometry
in these minima is practically the same as for gas phase
ethane, and the well depths are shallow. However, we do
not consider it appropriate to analyse the desorption
process further within the DFT approximation.

The two distinct pathways (TS1 and TS2) character-
ised for C2H6 dehydrogenation, sample the geometric
corrugation of the metal surface with the C–H bond that
breaks approximately aligned along the [110] or the
[100] directions. For these processes, the C–H bond
length extends to a value of 1.45 and 1.57 Å for TS1
and TS2, respectively. The activation barriers for the
two processes are similar: 0.38 and 0.42 eV, in agree-
ment with our finding of isoenergetic barriers for CH4
dehydrogenation over the same surface [20]. In the pro-
duct coadsorbed state, the C2H5 moiety resides preferen-
tially at a ridge atop site, whilst the location of the H
atom immediately after dissociation depends upon the
TS state involved. The H atom sits at a threefold-coor-
dinated fcc site for pathway TS1 and at a twofold-coor-
dinated bridge site for pathway TS2. Furthermore, the
product state for pathway TS2 is 0.09 eV higher in
energy than for TS1, suggesting that electronic stabilisa-

The current theoretical results suggest that excitation
of stretch and deformation vibrational modes, as well as
increasing translational energy in the reactant gaseous
C2H6 state, should enhance the rate of dehydrogenation
via pathways TS1 and TS2. In their supersonic mole-
cular beam study Harris et al. [15] postulated three distinct
mechanisms for C2H6 dissociation on Pt\{110\} at a sur-
face temperature of 600 K, depending on the incident
translational energy of the gaseous C2H6. For transla-
tional energies, Ei, less than 0.2 eV, they concluded that
dissociation is activated and assisted by excitation of the
C–H stretch modes. For Ei in the range 0.2–0.4 eV, the
dissociative sticking probability, s
i, was found to be
independent of translational energy, but increased with
excitation of the asymmetric deformation modes, as in-
ferred from an Arrhenius plot, whilst for Ei > 0.4 eV,
dehydrogenation was found to increase with both trans-

In this picture, diffusion of physisorbed C2H6 to
the ridge and Pt adatoms in the troughs of the surface, which might not
behave very differently. More reactive Pt adatom defects
are likely to be present at the \{111\}-like interface region
joining any two large domain \{110\} terraces on an experimen-
tal Pt\{110\} crystal.

Even if the concentration of reactive defects is around
1\%, a moving C2H6 molecule hitting the surface is more
likely to strike at defect-free sites. The experimental
results suggest that for C2H6 incoming translational en-
gies below 0.16 eV the latter process must first involve
the physical adsorption of C2H6, followed by disso-
ciation. In this picture, diffusion of physisorbed C2H6 to
a defect site could also lead to dissociation. For this
hypothetical process, vibrational excitation in the
incoming molecule would lead to a decrease in trapping
probability, as a greater fraction of vibrational energy
must be dissipated to the surface for trapping to occur,
in agreement with experiment. As the translational en-
gy is increased from 0.16 to 0.42 eV, decreasing contrib-
utions to the sticking probability arise from trapping.
However, a concomitant rise in the sticking probability
for direct C2H6 dissociation over activated barriers takes
place. Within this picture, the upper 0.42 eV bound may
imply that for these translational energies dissociation occurs mainly via direct activated processes, which would agree with our calculated barriers of 0.38 and 0.42 eV (see Fig. 3).

Pathway TS3 involves β-hydride elimination of C$_2$H$_5$ to ethene (H$_2$C–CH$_2$). The C–C axis is approximately aligned along the [110] surface direction in the reactant state. Tilting of the C–C bond and elongation of a C–H bond pointing directly downwards at the surface then leads to the TS, and from there to the formation of di-σ bonded H$_2$C–CH$_2$. If the C–C axis is approximately aligned along the [100] surface direction, however, diffusion of the C$_2$H$_5$ species from an atop to its adjacent bridge site along the ridge leads to the formation of adsorbed ethylidene (HC–CH$_3$) via pathway TS4. Again, the activation barriers for these two distinct processes,
which can also be regarded as sampling the corrugation of the surface, are of similar magnitude: 0.29 and 0.33 eV, respectively. In a future paper we will report barriers to further dehydrogenation, which will allow us to describe the thermal behaviour of our system with increasing surface temperature. Since we find the barriers to further dehydrogenation of C₂H₄ species to be larger than 0.40 eV, kinetic considerations suggest that

<table>
<thead>
<tr>
<th>Path</th>
<th>E₁</th>
<th>ΔE₁</th>
<th>Eₜₛₜ</th>
<th>ΔE₂</th>
<th>E₂</th>
<th>Eigenvalue</th>
</tr>
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<tbody>
<tr>
<td>TS1</td>
<td>0.22</td>
<td>0.38</td>
<td>0.60</td>
<td>0.60</td>
<td>0.00</td>
<td>-4.46</td>
</tr>
<tr>
<td>TS2</td>
<td>0.18</td>
<td>0.42</td>
<td>0.60</td>
<td>0.51</td>
<td>0.09</td>
<td>-4.13</td>
</tr>
<tr>
<td>TS3</td>
<td>0.46</td>
<td>0.29</td>
<td>0.75</td>
<td>0.75</td>
<td>0.00</td>
<td>-3.30</td>
</tr>
<tr>
<td>TS4</td>
<td>0.46</td>
<td>0.33</td>
<td>0.79</td>
<td>0.64</td>
<td>0.15</td>
<td>-3.66</td>
</tr>
</tbody>
</table>

Energies are in eV. The energy of the lowest minimum for the paths corresponding to TS1 and TS3 was chosen as the arbitrary zero for C₂H₆ and C₂H₅, respectively. E₁ and E₂ are the energies of the higher and lower minimum for each path, Eₜₛₜ is the energy of the TS, and ΔE₁ and ΔE₂ are the corresponding barriers. The final column gives the unique negative Hessian eigenvalue at the transition state in eV Å⁻².
both ethene and ethylidene species will form in approximately equal amounts on the surface at low surface temperatures.

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References